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27 Abstract: The Adsorption and filtration of waste water in an isothermal column of granular activated ~~column~~ carbon has been mathematically modeled. Based on this model, a simulation program was prepared and coded in Fortran IV to be run on the IBM 360/50 level G compiler. A separate companion study was conducted on the filtration of a clay suspension in an activated carbon bed to provide a filtration rate equation. The equation so obtained was then assumed to represent the filtration rate equation of the wastewater. Adsorption, the, was considered to be controlled by a combination of liquid phase diffusion and intraparticle diffusion. These two phenomena were then approximated by a solid phase rate expression based upon Glueckauf's linear driving force. In addition to adsorption and filtrations, the effects of backwashing and regeneration were also included in the model. A newly developed algorithm was used for the numerical integration of the pertinent characteristic normal hyperbolic equations. The design of the program allowed a clear separation of calculation framework and column model. This separation was made to permit new discoveries and new theories to be adapted to the basic program with minimal difficulty. The incompleteness and uncertainty of current theories of the carbon contact process will almost certainly make the ease of adaption the most important feature of the program. (Lowry-Texas)

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CARBON COLUMN OPERATION IN WASTE WATER TREATMENT

by

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for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

Project #17020 DZO

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ABSTRACT

A mathematical model has been devised to simulate the adsorption and filtration of waste water in an isothermal column packed with granular activated carbon. The adsorption process is considered to be controlled by a combination of liquid phase diffusion and intraparticle diffusion which can be approximated by a solid phase rate expression based upon Glueckauf's linear driving force. The filtration rate equation is assumed to be the same as that of filtration of clay suspension in a carbon bed, which was investigated experimentally as a companion study of this work. In addition to adscrption and filtration, the effects of column backwashing and carbon regeneration are included in the model. A newly developed algorithm (discussed in detail in Part IV of this final report) is used for the numerical integration of the pertinent characteristic normal hyperbolic equations. With this algorithm, an industrial column of 20 feet height operating a one-hundred day period can be simulated with less than 10 minutes of IBM 360/50 computer time giving two decimals or better accuracy.

Based on this model, a simulation program is prepared and coded in FORTRAN IV to be run on the IBM 360/50 level G compiler. A unique feature of this program is the clear separation of calculation framework and model for the column behavior. Thus, it is possible, for example, to adapt the present program to a variety rate expression and adsorption isotherm, which are not considered in the present model. This is especially important in view of the incompleteness and uncertainty about our understanding of the carbon contacting process in waste treatment and the likely new discovery to be made in the future.

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I. INTRODUCTION

The use of activated carbon for the removal of contaminants has been known for a long time and its use has been traced back to almost three thousand years ago [H-3]. In terms of water purification, activated carbon has been used primarily for the removal of odor and color even though some pioneer work was carried out as early as 1931 [G-1, H-2, B-1] in which the granular activated carbon was used for sewage treatment.

The presence of excessive refractory material in lakes and rivers caused much anxiety on the part of the public during the early part of 1960. The concern prompted renewed interest in the use of activated carbon for the removal of organic contaminants. Weber and Morris [W-1] conducted batch experiments on the adsorption of ABS (Alkyl Benzene Sulfate) onto granular activated carbon and feasibly studies involving column operation with secondary effluent were made by Joyce and Sukenik [J-1] and Bishop et al [B-3]. At approximately the same time, large scale pilot plant and demonstration plant work of treating waste water with granular activated carbon were initiated (and still in progress) at several places, notably Lake Tahoe [C-9, C-10] and Pamona of Los Angeles County Sanitation District [E-1, P-3] under the auspices of the Federal Water Quality Administration. The application of carbon treatment in these studies is considered as a critical step in the tertiary treatment process for the removal of organic contaminants. This removal is deemed essential for complete water renovation as well as necessary preparation for further treatment such as reverse osmosis.

A most significant development in the application of carbon treatment for waste water has taken place recently. In their demonstration plant work at Washington, D.C., a new process named IPC (Independent Physical Chemical Treatment) was developed, in which the raw sewage is treated in a process consisting of clarification, filtration, ion exchange and carbon adsorption. The quality of the IPC process is found to be superior to that obtained from conventional-tertiary treatment. The IPC treatment gives better removal of contaminants of every category. In addition, there are two distinct advantages: (1) The land requirement of the treatment plant based on IPC process is far less than that of the conventional plant.

This is most important for some metropolitan areas where available land is already scarce. (2) The IPC process can be operated at fairly low temperatures while the conventional plant which requires biological treatment is inevitably temperature-dependent. The development of IPC would, therefore, be most important in the area such as Alaska and the Artic region where the waste disposal problem poses the most severe challenge to the regions' future development. Beyond these applications, carbon adsorption can be applied for industrial waste treatment. Experimental evidences abound in literature which indicates the successful removal of organic substance such as phenols, fatty acids, insecticides and pesticides by carbon adsorption.

In spite of the very promising feature of the carbon process for waste treatment, many problems remain to be solved before its application can be put in general practice. One of the major concerns is its relatively high cost, which has been estimated to be varying from 10 $\sim$ 15¢ per thousand gallons as a tertiary treatment step [C-7]. Other than the possibility of obtaining carbon at a lower cost through the improvement of its manufacturing, a significant reduction of the cost can be achieved by the improvement of the process itself. This requires further pilot plant work as well as process simulation.

The object of the present study is to devise a mathematical model which will simulate the dynamic behavior of the carbon column in waste water treatment. Much of the basic information about the carbon contact process was obtained as parts of the overall work in carbon column operation, and are described in detail in Parts II and III of this report.

In terms of its ultimate purpose, a model, when perfectly constructed, should provide a rational basis for design optimization and process control. Such a claim, however, cannot be made to the present model. Rather, the present model is intended (1) to show the efficacy of modelling by indicating what experiments are urgently needed and (2) to examine, by confrontation with adequate data what modifications are required to make the model more reliable. Only when these have been accomplished, can meaningful design studies be undertaken.

II. CARBON COLUMN OPERATION IN WASTE WATER TREATMENT - A GENERAL CONSIDERATION

For the removal of organic contaminants from waste water column operation with granulated activated carbon represents only one of the many possible contacting processes. Other possibilities include the fluidized bed process considered by Weber and his collegues [W-4, K-1], but at present the economics of such a system appear less promising than a fixed-bed process. Such fluidized columns tend to be unstable and difficult to control. They require higher capital and operating costs. Furthermore, the usual advantages of fluidized bed operation will probably not be realized in this system. Due to agitation and particle motion, the transport of adsorbate to the particle surface will be facilitated in a fluidized bed. However, a significant increase in mass transfer rates will only result if the liquid side resistance is rate-limiting. For solid/liquid adsorption systems, and, in particular, for activated carbon/water/organics, many experiments indicate that intraparticle diffusion is the limiting rate process [E-1, A-2, S-2, W-3, D-2, M-1, S-1, W-2]. Weber and Keinath [W-4, K-1], do not agree with this conclusion. Weber himself has recently compared the performance of fixed and expanded beds in a pilot plant at Ewing-Lawrence, New Jersey [W-5]. Although the difference was not large (about 2.5%) over a four month period, the fixed beds gave consistently purer effluents. One advantage of fluidization cannot be denied: backwashing of the beds is obviated [W-5]. However, this may well be at the expense of effective filtration.

Another type of contacting process involves the use of powdered carbon. In general, the powdered carbon is first mixed with waste water in a large tank, then filtered and discarded. If recent pilot plant studies on a regeneration process for powdered carbon prove successful, then usage of such a powder may become economically attractive. However, efficient regeneration of granular carbon is already a proven process [C-9]. Furthermore, continuous treatment of waste water in a column packed with active carbon makes more efficient use of the carbon. Fresh waste water first contacts the most nearly spent carbon particles, thus allowing a closer approach to its adsorption capacity. Using downflow contactors,

III. FORMULATION OF MODEL

(III-A) Modelling Consideration - Waste Water System

Since the function of the carbon column process is the removal of undesirable contaminants, the characterization of these contaminants becomes necessary before a quantitative description of the removal process can be formulated. The large variety of contaminants which are likely to be present in waste water and their minute amounts, make it impossible for individual identification and traditionally these wastes can only be represented by gross overall concentration variables such as BOD, COD, or TOC which is used in the present modelling work. The use of TOC (total organic carbon) for characterizing waste concentration is a convenient one because of the commerically available instrument [Beckman TOC Analyzer] which can be used to obtain TOC values from a sample waste water with reasonable ease. Some earlier work, however, has employed the use of COD (chemical oxygen demand). It is also necessary to make a distinction between the two mechanisms responsible for the removal of contaminants from waste water in the adsorption process and the filtration process. For this investigation, we shall assume that the TOC of a waste water sample represents the sum of the DOC (dissolved organic carbon) and SOC (suspended organic carbon). The former is removed by adsorption into the carbon granule while the latter is removed by deep bed filtration.

The use of a single gross quantity, DOC, for the description of an adsorption process is tantamount to the approximation of a multi-solute system by a pseudo single solute system. The validity of this assumption can be only tested through experimental confirmation.* At best, this can only be considered as an approximation.

As part of our overall program on the study of carbon column operation, experimental results on batch adsorption of waste water (secondary effluent)/ granular activated carbon were obtained and interpreted on the basis of a pseudo single-solute assumption. The experimental results, to a degree, substantiate the validity of this assumption and the numerical values of

---

*Experimental confirmation is obtained if one can obtain experimentally a consistent adsorption isotherm based upon DOS, and a successful interpretation of adsorption kinetic data of waste water/activated carbon consistent with the pseudo single solute assumption.

the pertinent parameters obtained experimentally are used in the column simulation. The detailed description of experimental work is given in Part II of this report.

(III-B) Modelling Considerations - Packed Columns

The chemical reactor, and, in particular, the packed tubular reactor, has been a subject of central concern to chemical engineers for many years. Comprehensive reviews of the state-of-the-art in the early 1960's have been given by Beek [B-2] for the design of steady-state, nonisothermal, catalytic reactors and by Wilhelm [W-6] for the transient problem as well. In 1970, Hlavacek [H-5] summarized the steady-state aspects, and Paris and Stevens [P-2] examined the methods and assumptions used for time-dependent problems. We select from these four reviews two major trends of the last decade: an increased interest in the Deans-Lapidus finite-stage or mixing-cell model [D-1, M-2] and a demand for practical computation times. The former of these regrettably turns out to be incompatible with the latter.

In principle, a packed tubular reactor has at least four independent variables: axial distance from the reactor inlet, radial distance from the reactor wall, radial distance measured from the surface to the centre of each porous granule, and time. Now, the brutal facts of present-day compuation are as follows:

a) A useful simulation program, to be run many hundreds of times, must not require more than a few minutes of computer time.

b) For virtually all processes of industrial size, on most available computers, this time constraint means that no more than two independent variables can be dealt with.

It will be shown that the two radial distances are the logical variables to neglect. This implies the negligence of radial dispersion of the column and the approximation of intraparticle diffusion by somewhat simpler expression.

First, consider the mixing-cell model previously mentioned. The original idea of simulating a packed column by a finite number of perfectly-stirred tanks in series is generally attributed to Kramers and Alberda in 1953 [K-2] in connection with tracer studies of longitudinal

dispersion in fixed beds. Deans and Lapidus [D-1] extended this concept to include radial dispersion by postulating a two-dimensional, staggered array of tanks.* Agreement with experimental data is quite good if the size of each tank (both thickness and depth) is of the order of one particle diameter. Dispersion parallel to the axis is simulated by complete mixing within each tank, and normal to the axis by splitting each CSTR** effluent into two streams which become influents to the adjacent tanks below. Backmixing, in the sense of downstream tanks affecting upstream tanks, cannot occur. This model is perhaps the best physical representation available for packed beds, and could be made even better by the incorporation of non-ideal stirred tank features such as incomplete mixing (Cholette, Cloutier and others [C-2, C-3, F-1]), and dead space interactions [C-5, C-6[. Lewich and others [B-4, L-1] have already used this latter idea to model ispersion in a porous medium.

Realistic as it may be, the cell model takes far too much computer time to be used for transient calculations. McGuire and Lapidus [M-2] have carried out such calculations for the stability of a nonisothermal packed bed reactor with a diffusion equation describing intraparticle effects.*** For a reactor 5 particles wide by 15 particles deep it required 3 hours of IBM-7090 time to simulate a flow of 13 reactor residence time units. A carbon granule size of 8 x 30 mesh would give about 500 particles per foot, so that a typical industrial waste water treatment column (based on Cover's 1970 design [C-8]) might involve 23,000 x 13,000 particles over at least 1000 bed residence times. Not only is the estimated calculation time ridiculous, but even with the removal of the heat transfer effects, the intraparticle effects, and the radial effects, and making allowance for much larger time steps, the estimate still amounts to hundreds of hours!

As another example, Feick and Quon [F-2] have simulated the transient behavior of a packed bed reactor with axial and radial dispersion using

---

*Every tank has an annular shape, with the same annular thickness and depth.

**CSTR = Continuous Stirred Tank Reactor

***This is a partial differential equation, whereas each CSTR is governed by an ordinary differential equation.

the more orthodox homogeneous dispersion model and a modified, alternating direction, explicit, finite difference procedure. Their reactor was 10 catalyst particles wide by 50 catalyst particles deep, and the simulation lasted for 2.5 reactor residence times. The computation on an IBM 360/67 took between 3 minutes and 90 minutes, depending on whether an intraparticle diffusion equation was used or not. This is an improvement of perhaps a factor of 10 over the cell model, chiefly on account of the larger spatial grid, but such a model is nevertheless entirely impractical for carbon column simulation. Because of these considerations Paris and Stevens [P-2] stated that most industrial-scale packed columns operating in a transient mode cannot be simulated with anything more complex than a plug flow model.

Having decided this on computational grounds alone, it should be added that the plug flow model happens to be a reasonably sound physical representation of both adsorption and filtration in fixed beds. Carbon columns are usually operated at a particle Reynolds number of about 2, which implies an axial Peclet number of about 2 from Wilhelm's correlation [W-6]. The axial dispersion will be small, and Beek [B-2] recommends that it be ignored under similar circumstances. Carberry and Wendel [C-1] estimate that there will be no significant axial effects beyond 50 particle diameters. Since the carbon columns operate isothermally, it is also a good assumption that the concentration profile has no radial variations. A note of caution is needed here, however. Since the length-to-diameter ratio of industrial columns is only about two or even less, complete radial mixing will not occur. If the flow distribution near the column inlet is particularly uneven, or if the packing of the granules has large voidage variations*, then radial concentration gradients could arise. This possible complication, however, will not be considered in the present work.

(III-C) Adsorption Process

It is felt that the adsorption of DOC is controlled by at most two mechanisms: transfer through the liquid phase to the exterior of the granule and intraparticle diffusion. Other mechanisms such as surface

*Haughey and Beveridge [H-4] have recently reviewed the structural properties of packed beds.

attachment is ruled out. Furthermore, the intraparticle diffusion is believed to be the dominant mechanism in view of the very low values of diffusion coefficients evaluated experimentally.* The liquid side transfer is only important where the carbon granule is fresh or under certain special conditions.**

If a unit volume of the packed bed is taken as a basis, the liquid-side transfer rate can be written as

$$\frac{\partial M}{\partial t} = \rho_\beta \frac{\partial q}{\partial t} = k_\ell \cdot f_1(cc^*) \qquad \text{(III-1)}$$

where ρ_β is the bulk density of granular carbon, of the solid phase concentration of the adsorbate (DOC). k_ℓ is defined as the liquid side mass transfer coefficient. The function $f_1(cc^*)$ represents the proper driving force. c* represents an effective liquid phase concentration of DOC adjacent to the granule surface.

Mass transfer within the granule apparently takes place by combination of force and surface diffusion mechanisms [D-2]. A proper treatment of the pertinent diffusion equation, in general, requires the numerical integration in a time-space grid.*** As mentioned earlier, the practical demand on the economy of computer time rules out the consideration of more than two independent variables for carbon column modelling. Approximation must, therefore, be used to represent this intraparticle diffusion by a simple rate expression. Hence,

$$\frac{\partial q}{\partial t} = k_s \cdot f_2(q,q^*) \qquad \text{(III-2)}$$

where k_s is the solid phase transfer coefficient and f_2 represents the proper driving force. q* is the solid phase concentration adjacent to the granule's exterior surface.

---

*See discussion in (VI-C).

**For example, the result of filtration may effect the coating of the carbon particle with a layer of slime and thus greatly increase the mass transfer resistance in the liquid side.

***Space, in this case, refers to that within the carbon granule.

Combining Equations (III-1) and (III-2), one has

$$k_\ell \cdot f_1(c,c^*) = \rho_\beta k_s f_2(q,q^*) \qquad \text{(III-3)}$$

If the equilibrium condition is maintained and the solid-liquid interphase (i.e. granule's exterior surface), one has

$$q^* = f_3(c^*) \qquad \text{(III-4)}$$

where f_3 is the adsorption isotherm of the system -- waste water-activated carbon expressed in terms of dissolved total organic carbon.

(III-D) Biochemical Effects

This perhaps is the least-known aspect of carbon column operation. Biological reactions can, in principle, affect the TOC level for each of the four concentration variables. Such reactions can be described rather crudely as follows:

[Dissolved Oxygen] + [Biodegradable TOC] + [Bacteria] = [Oxidation Product] + [More Bacteria]

Since the oxidation product usually includes CO_2 only, the net effect is to decrease the TOC level. Most of the rate data for such reactions come from BOD studies on closed systems. Both first and second order rate expressions have been suggested [R-1, Y-1] and possess roughly equivalent predictive values.

The biodegradable TOC are present in both the dissolved organic contaminants as well as the suspended matters. Since both types of substances can be either in liquid or solid phase, four distinct reactions are possible. This includes the degradation of suspended organic carbon (SOC) in liquid phase, of SOC in solid phase, of dissolved organic carbon (DOC) in liquid phase and of DOC adsorbed in solid phase. The last kind of reaction perhaps is not likely to occur if we consider the relative size of the carbon particle pore and the average bacteria. The first three kinds of reaction rates designated as R_c, R_y and R_σ can be assumed to be

$$- R_c = k_{\beta_1} f_5 \left[(c-c_n), \{O_2\} [\text{Bacteria}] \right] \qquad \text{(III-5)}$$

$$- S_2 = k_{\beta_2} f_6 \left[(y-y_n), \{O_2\} \text{ [Bacteria]}\right] - d_1 R_c \qquad \text{(III-6)}$$

$$- R_\sigma = k_{\beta_3} f_7 \left[(\sigma-\sigma_n), \{O_2\} \text{ [Bacteria]}\right] \qquad \text{(III-7)}$$

where the subscript n denotes the non-biodegradable part of the contaminant, and σ the volume fraction of the suspended matters deposited on to the carbon bed. The k_β's are rate constants. The term $d_1 R_c$ of Equation (6) accounts for the possible increase in suspended matters due to the degradation of DOC.

(III-E) Filtration Effects

To complete the description of the dynamic behavior of a carbon column, the filtration rate needs to be given. In general, on a volume basis, the rate of deposition, S_1 of the filtration process is given as

$$S_1 = K_o f_4(\sigma, y) \qquad \text{(III-8)}$$

where K_o is often referred to as the impediment modulus or the filtration coefficient. The relationship between the deposition rate, the possible biological degradation of deposited suspended matters S_2 (or R_σ) and the rate of change of deposited matter in the carbon column, $\frac{\partial \sigma}{\partial t}$, is given as

$$\frac{\partial \sigma}{\partial t} = K_o f_4(\sigma, y) - R_\sigma \qquad \text{(III-9)}$$

IV. MATHEMATICAL EQUATIONS DESCRIBING THE DYNAMIC BEHAVIOR OF COLUMN OPERATION

(IV-A) Basic Equations

Based upon the plug flow and other assumptions stated in (III-B), the continuity equations describing the adsorption of dissolved TOC and the filtration of suspended matters can be written, respectively, to be:

For Adsorption

$$u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + \rho_B \frac{\partial q}{\partial t} - R_c = 0 \qquad \text{(IV-1)}$$

For Filtration

$$u \frac{\partial y}{\partial z} + \varepsilon \frac{\partial y}{\partial z} + S_1 - S_2 = 0 \qquad \text{(IV-2)}$$

where

z = axial distance measured from the column inlet

t = time

u = superficial velocity

ε = fraction of interstitial voids in packing

and meanings of the symbols are the same as before.

Equations (IV-1) and (IV-2) are the basis for column simulation. The specification of certain terms that appear in these two equations, however, are needed. This will be discussed in the following section.

(IV-B) Adsorption Rates

The equations describing the adsorption rates are given by Equations (III-1), (III-2) and (III-4)

$$\frac{\partial q}{\partial t} = \frac{k_\ell}{\rho_B} f_1(c,c^*) \qquad \text{(III-1)}$$

$$\frac{\partial q}{\partial t} = k_s f_2(q,q^*) \qquad \text{(III-2)}$$

$$q^* = f_3(c^*) \qquad \text{(III-4)}$$

Equation (III-4) represents the adsorption isotherm of the system of waste water/granular activated carbon on the basis of single-solution

assumptions and the representation of organic contaminant concentration with DOC (dissolved organic carbon). The adsorption isotherm data was obtained as part of our study and the experimental work was described in Part II. In general, the Freundlich's adsorption isotherm was found to represent the result reasonably well, i.e.

$$q^* = b_1 \cdot c^{*b_2} \qquad \text{(IV-3)}$$

Based on one series of experimental work, it was found from least square fit that

$$b_1 = 5.3217 \times 10^{16}$$

$$b_2 = 2.3243$$

On the other hand, from a computational point of view, it would be desirable that the exponent, b_2, should be an integer. A less accurate fit of the data yields

$$q^* = 1.3451 \times 10^9 \cdot c^{*2} \qquad \text{(IV-4)}$$

which gives a minimized sum of squares of .00089 in comparison to 0.00017 of Equation (IV-3). This difference is obviously not too serious and Equation (IV-4) is used in the simulation program.

The liquid film mass transfer coefficient, k_ℓ, can be estimated from the well established correlation, provided the granules' exterior surface remains clean. To make a distinction between the mass transfer coefficients corresponding to different surface conditions, the mass transfer coefficient for a clean surface is designated to be k_{ℓ_o}. The actual mass transfer coefficient k_ℓ may or may not be the same of k_{ℓ_o}. This is to be discussed under Section (IV-E).

From Perry's Handbook, [P-4], we have

$$k_{\ell_o} = 2.12 \, (D_f u_o)^{1/2} \, d_p^{-3/2} \qquad \text{(IV-5)}$$

By examining the diffusivities of various organic molocules in water, it is estimated that k_{ℓ_o} shall lie between $10^2 \sim 10^3$ hr.$^{-1}$.

To consider the intraparticle diffusion properly, the pertinent diffusion equation should be solved. This, however, is not practical as pointed out earlier. Instead, a simplified approximation in terms of a solid phase mass transfer coefficient will be used. In connection with this concept, two types of driving forces have been suggested. They are:

$$\frac{\partial q}{\partial t} = k_s(q^*-q) \qquad \text{(IV-6)}$$

according to Glueckauf's linear driving force [P-1], and

$$\frac{\partial q}{\partial t} = k_s(q^{*2} - q^2)/(2q - q_o) \qquad \text{(IV-7)}$$

according to Vermeulen [V-3]. When q_o is the initial solid phase concentration, Equation (IV-6) is used because of its simpler form. The solid phase mass transfer coefficient, k_s, is related to the intraparticle diffusion coefficient, D_s, by the following expression [V-2]:

$$k_s = 15\ D_s/d_p^2 \qquad \text{(IV-8)}$$

Experimental work has been carried out to evaluate D_s based on pore diffusion and solid diffusion model (see Part II). The studies indicate that D_s lies between $10^{-10} \sim 10^{-9}$ cm^2/sec.

(IV-C) Biochemical Reaction

At the present time, it is not possible to formulate even in the most crude form, the functional form of f_5, f_6 and f_7 [see Equations (III-5) - (III-7)]. Consequently, the biochemical effect cannot be considered in our model. A few qualitative comments may be in order. Generally speaking, both R_c and R_y are perhaps of secondary importance. The data on blank waste water decay reported in Part II of this report seems to substantiate this point of speculation. The term R_σ is more important and the decay of deposited organic matter perhaps explains what was observed by Bishop and co-workers [B-3].

A quantitative expression of R_σ obtained from direct experiment is not available, and quite likely, will remain to be so for sometime to come. The culprit of this is that some of the important parameters in biological action such as dissolved oxygen concentration, bacteria species and population are not fixed quantities but of random nature. The determination, therefore, will require some ingenious experimentation.*

Because of the lack of basic data, the biological terms will be neglected in the preliminary work. The importance of these terms can be discussed indirectly by comparing the simulated result with negligible biological effect with actual performance data when these effects are known to be pronounced. It may be possible that through such trial and error procedure, a crude expression of R_σ may be obtained.

(IV-D) Filtration Rate

Most of the previous work on the filtration studies use sand filters as "synthetic waste". Consequently, we have carried out experimental work of the filtration of clay suspensions through a carbon bed (see Part III of the report). The empirical rate was found to be

$$S_1 = K_o f_4(\sigma, y) = (K_o) \cdot f_4(\sigma) \cdot y \qquad \text{(IV-9)}$$

$$f_4(\sigma) = \frac{1}{(1 + \gamma\sigma)^n} \qquad \text{(IV-10)}$$

Assuming that values K_o, γ and n obtained from clean beds are applicable for actual column operation when the granular carbon is used over a prolonged period of time. Another important consideration is the estimation of the increase of pressure drop during filtration, which determines the frequency of backwashing. Our work on pressure drop, as reported in Part III, suggested the following simple expression relating the increase of pressure drop with the amount of particle deposition.

$$\left(\frac{dp}{dz}\right) / \left(\frac{dp}{dz}\right)_o = 1 + \delta\sigma \qquad \text{(IV-11)}$$

---

*It may be necessary to radioactively tag the suspended matters and, therefore, to be able to monitor what happens to the deposited matter.

(IV-E) Interactions Between Adsorption and Filtration

The original adsorption and filtration models suggested in Sections (III-C) and (III-E) are independent of each other. Interactions can occur from at least two sources. The first is the biochemical Equations (III-5), (III-6) and (III-7). It is possible that substrate in the form of dissolved matter may be in competition with the suspended solids for available oxygen. Furthermore, oxidation of dissolved TOC could conceivably produce additional filterable material.

The filtration process may affect the adsorption in another way, because the deposited solids tend to form a sheath around the granules, thus hindering the liquid-side mass transfer. To simulate this, the liquid-side mass transfer coefficient is made a function of retention,

$$k_\ell = k_{\ell_o} f_\beta(\sigma) \qquad \text{(IV-12)}$$

If the dependence of function of f_β is taken as linear, so that

$$k_\ell = k_{\ell_o}(1 - r_d\sigma) \qquad \text{(IV-13)}$$

where

r_d = retention degradation of k_ℓ

The value of r_d is unknown, but it should be sufficiently large so that k_ℓ can be reduced by say 50% when the carbon granule is fully coated. Since the largest reported values of σ are about 0.05, the minimum value of r_d is 10, and this has been used extensively in our model.

(IV-F) Effect of Backwashing

As filtration proceeds, the pressure required to pump water through the carbon columns increases until backwashing is necessitated. The simulation must include:

(a) the criteria for backwashing, and

(b) the effect of backwashing.

With regard to (a), backwashing may be carried out at regular intervals. For example, at Pomona [P-3] it was carried out at 24 hour intervals, and at Ewing-Lawrence [W-5] every 60 hours. On the other hand, the real

physical criterion is the maximum head-loss that the pumping system can reasonably maintain. This will differ from installation to installation; a typical figure from Pomona is one psi per foot of carbon. The present model is defined either to backwash at regular intervals, or to backwash automatically when a certain pressure drop maximum is reached.

With regard to (b), not much is known about the physics of backwahsing. It is the filtration problem in reverse: to find the effluent distribution and retained solids distribution when an initially dirty bed is washed with relatively clean water.

The columns are, of course, backwashed in the reverse direction to the normal flow. The flow rate is usually high enough to expand the bed by 30% to 50% of its normal height. The extent of axial mixing (of granules) is unknown, but it may be quite small. It is clear from the Lake Tahoe reports [C-9] that the backwashing is never complete. Heavily coated granules retain a thin layer of slime from backwash to backwash and this may eventually prevent further adsorption, even though the carbon is not fully saturated. The opposite effect has also been suggested [P-3], in which the slime layer participates in biological oxidations and increases the apparent adsorptive capacity of the carbon.

For lack of better information, our model assumes that backwashing removes a constant fraction of the retained solids (the remaining fraction is called the slime residue factor (SRF) and has been set at 0.05 throughout most of the initial simulation runs. Thus, the slime profile has a similar shape to that of the retained solids, but a smaller magnitude. It is assumed that the backwashing does not alter the distribution of adsorbed TOC (q) in the column, and in Model I only the first section of the column may be washed.

(IV-G) Effect of Regeneration

The main questions about regeneration concern the quality of the treated carbon granules. Is the adsorption capacity unchanged? Are the filtration parameters the same? And so on. As far as adsorption is concerned, the carbon appears to have undiminished capacity*, and in our model the same assumption is amde for all the other parameters, including

*There is maybe some loss of capacity on the first few cycles, but this levels out.

filtration.

It should be clear that the regeneration process itself is not simulated (unlike bachwashing). All that is done in our model is to remove the first section of the column, and add a new section of fresh carbon after the last section. The criteria for this operation are very similar to those for backwashing. Regeneration may take place either at fixed intervals, or when the effluent TOC concentration from the last section of the column passes a certain specified limit, whichever condition arises first. The "effluent TOC" in this case refers to the combined effects of dissolved organic pollutants and suspended solids. This means that a "suspended solids conversion factor" is needed to express volumes per volume of suspended solids as grams of TOC per unit volume of waste water (SSCF $\sim$ 1.0 gm/cc). In the case of backwahsing and regeneration being called for at the same time, regeneration will have the priority.

(IV-H) Summary of Equations and Associated Conditions

When all these assumptions stated above are invoked, the system of equations describing the column behavior is found to be:

$$u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + k_{\ell_o}(1 - r_d\sigma)(c - c^*) = 0 \qquad \text{(IV-14)}$$

$$\frac{\partial q}{\partial t} = k_s(q^* - q) \qquad \text{(IV-15)}$$

$$k_s = 15\ D_s/d_p^2 \qquad \text{(IV-16)}$$

$$q^* = b_1 c^{*2} \qquad \text{(IV-17)}$$

$$k_{\ell_o}(1 - r_d\sigma)(c - c^*) = \rho_B k_s(q^* - q) \qquad \text{(IV-18)}$$

$$u \frac{\partial y}{\partial z} + \varepsilon \frac{\partial y}{\partial t} + \frac{K_o y}{(1 + \gamma\sigma)^n} = 0 \qquad \text{(IV-19)}$$

$$\frac{\partial \sigma}{\partial t} = \frac{K_o y}{(1 + \gamma\sigma)^n} \qquad \text{(IV-20)}$$

$$\frac{\partial P}{\partial z} = \left(\frac{\partial P}{\partial z}\right)_o (1 + \delta\sigma) \qquad \text{(IV-21)}$$

The concentrations c, q, y and σ are made dimensionless in the following manner:

$$C = c/c_o \qquad \text{(IV-22)}$$

$$Q = q/(b_1 c_o^2) \qquad \text{(IV-23)}$$

$$Y = y/y_o \qquad \text{(IV-24)}$$

$$S = \sigma \qquad \text{(IV-25)}$$

where the subscript "o" indicates an input concentration to the first section of the column at the start of the simulation. With these transformations, Equations (IV-17) and (IV-18) become

$$Q^* = (C^*)^2 \qquad \text{(IV-26)}$$

and

$$Q^* = Q + N_2 f_8 (C - C^*) \qquad \text{(IV-27)}$$

where N_2 is defined below, and

$$f_8 = 1 - r_d S \qquad \text{(IV-28)}$$

By solving Equations (IV-26) and (IV-27), it is found that

$$C^* = \frac{1}{2}\left\{- N_2 f_8 + \left(N_2^2 f_8^2 + 4(Q + N_2 f_8 C)\right)^{1/2}\right\} \qquad \text{(IV-29)}$$

where the positive root has been chosen. The equations are then converted to dimensionless characteristic normal form by the following transformation:

$$T = k_s(t - \varepsilon z/u) \qquad \text{(IV-30)}$$

$$Z = z/L \qquad \text{(IV-31)}$$

where L is the total length of column sections in series. An additional assumption is made that the mean superficial flow velocity and the voidage remain constant at their initial values u_o and ε_o. The resulting

system is

$$\frac{dC}{dZ} = - N_1(1 - r_d S)(C - C^*) \qquad \text{(IV-32)}$$

$$\frac{dQ}{dT} = N_2(1 - r_d S)(C - C^*) \qquad \text{(IV-33)}$$

where C* is taken from Equation (IV-29), and

$$\frac{dY}{dZ} = - N_3 \frac{Y}{(1 + \gamma S)^n} \qquad \text{(IV-34)}$$

$$\frac{dS}{dT} = N_4 \frac{Y}{(1 + \gamma S)^n} \qquad \text{(IV-35)}$$

$$\frac{dP}{dZ} = \left(\frac{dP}{dZ}\right)_o (1 + \delta S) \qquad \text{(IV-36)}$$

where

$$N_1 = L\, k_{\ell_o} / u_o \qquad \text{(IV-37)}$$

$$N_2 = k_{\ell_o} / (k_s \rho_B b_1 c_o) \qquad \text{(IV-38)}$$

$$N_3 = L\, K_o / u_o \qquad \text{(IV-39)}$$

$$N_4 = y_o K_o / k_s \qquad \text{(IV-40)}$$

The scale has been selected so that for a reasonable set of parameters all of the dimensionless variables and groups will be of order unity.

The boundary and initial conditions used with Model I are:

$$Q(Z,0) = 0 \qquad \text{(IV-41)}$$

$$C(0,T) = 1 \qquad \text{(IV-42)}$$

$$S(Z,0) = 0 \qquad \text{(IV-43)}$$

$$Y(0,T) = 1 \qquad \text{(IV-44)}$$

As discussed previously, these associated conditions represent the reactor inlet concentrations, and the initial solid phase distributions. In the general model, one might consider associated conditions

$$Q(Z,0) = f_9(Z) \tag{IV-45}$$

$$C(0,T) = f_{10}(T) \tag{IV-46}$$

$$S(Z,0) = f_{11}(Z) \tag{IV-47}$$

$$Y(0,T) = f_{12}(T) \tag{IV-48}$$

These generalized conditions would be quite easy to implement in the simulation. Either in the case of Equations (IV-41) to (IV-44) or (IV-45) to (IV-48), the missing conditions at the inlet and the tip of the plug have to be found by integration. These conditions are

$$\frac{d}{dZ}\{\ C(Z,0)\ \} = -\ N_1\ \{\ C(Z,0) - C^*\ \} \tag{IV-49}$$

where

$$C^* = \frac{1}{2}\{\ -\ N_2 + \{N_2^2 + 4N_2C(Z,0)\}^{1/2}\ \}$$

$$C(0,0) = 1$$

and

$$\frac{d}{dZ}\{\ Y(Z,0)\ \} = -\ N_3Y(Z,0) \tag{IV-50}$$

where

$$Y(0,0) = 1$$

and

$$\frac{d}{dT}\{\ Q(0,T)\ \} = N_2\ \{\ 1 - r_dS(0,T)\ \}\ \{1 - C^*\} \tag{IV-51}$$

where

$$Q(0,0) = 0$$

$$f_8 = 1 - r_dS(0,T)$$

$$C^* = \frac{1}{2}\{ - N_2 f_8 + \left[N_2^2 f_8^2 + 4 \{Q(0,T) + N_2 f_8\} \right]^{1/2} \}$$

and

$$\frac{d}{dT}\{ S(0,t) \} = \frac{N_4}{\{1 + \gamma S(0,t) \}^n} \qquad \text{(IV-52)}$$

where

$$S(0,0) = 0$$

It will be observed that only Equation (IV-49) can be integrated analytically. A similar set of initial and boundary conditions must be integrated after every backwash and regeneration.

CHAPTER V SIMULATION PROGRAM

For the convenience of subsequent discussion, we shall designate the model which we have constructed in this work as Model I and hopefully to continue this sequence of names as further improvements are made.

(V-A) Computation Algorithm. For Model I, Equations (IV-14) - (IV-21) provide the basis for the simulation of the dynamic behavior of carbon columns. The adsorption and filtration aspects of the operation are given by Equations (IV-32) - (IV-33) and Equations (IV-34) - (IV-35), respectively. Both set of equations, however, can be represented by the general form

$$(U_1)_z = \phi_1 (z, t, U_1, U_2) \qquad (V\text{-}1)$$

$$(U_2)_t = \phi_2 (z, t, U_1, U_2) \qquad (V\text{-}2)$$

where U_1 and U_2 are the dependent variables and z and t are the independent variables. The subscript refers to partial differentiation. For example, for adsorption, U_1 and U_2 are C and Q, respectively. Similarly for filtration, U_1 and U_2 become Y and S.

Equations (V-1) and (V-2) are known as semi-linear hyperbolic equations and they are frequently encountered in engineering applications. A number of computation algorithms based on methods of characteristics have been developed in the past for their numerical solution, (A-1), but were found unsatisfactory for the present application. The principal objection is the high computer time demand because of the large column size and the long period of operation in actual carbon column application.

An extensive study was undertaken by Vanier [V-1] for the development of new algorithms as part of the overall program. A particular algorithm designated by Vanier as CN553 was selected for the numerical integration of the adsorption and filtration equations. This algorithm was developed based on Taylor's series expansion and is of fourth order in local truncation error and third order in global discretization error. It also has the additional advantage of requiring less computation time in comparison to other algorithms. It should be pointed out that the simulation program developed here is not restricted

to the use of this particular algorithm. If for some reason another method of computation is preferred, it is only necessary to make a change in the appropriate subroutine. A brief description of the algorithm is given in Appendix B.

In addition to the adsorption and filtration equations, the initial conditions of C and Y for T = 0 and Q and S at z = 0 have to be calculated. This step, referred to as initialization, is carried out by the numerical integration of Equations (IV-49) and (IV-50) with respect to z and Equations (IV-51) and (IV-52) with respect to T. These integrations are made with a fourth order Runge-Kutta method.

(V-B) Program Structure The simulation consists of a main program and eight subroutines of which the method of characterization subroutines is the most important. The computation algorithm, designated as CN553 (see Part IV), is used. However, this can be changed with more accurate ones (fourth order is better) if this is warranted. A list of the subroutines and their functions are shown in Table 5-1.

The structure of the program is described by the flow charts in Figures (5-1) and (5-2). The main program reads and prints all the input data, and calls on ancillary processes such as backwashing and regeneration whenever needed. It also calls the method of characteristics subroutine (MOC) which thereafter controls the calculations. There is a clear separation of calculation framework and model. The model equations are contained in subroutine UZT and the equations for initial and boundary conditions in subroutines UZ and UT. To experiment with a new model, it is only necessary to change these three subroutines and the definitions of scale factors and dimensionless groups in the main program. Since the pressure equations are unlikely to be altered, these have been carried out in subroutine MOC. Experimentation at a lower level to investigate the effect of various parameters has been highly automated. The program will process sequentially a number of data sets, each representing an experiment with a new group of parameter values. Unchanged parameters need not be repeated in adjacent data sets, and the input is carried out with key words (example: CMAX = 7.0E-6)[1] and an otherwise free format.

---

[1]Standard FORTRAN notation: E-6 ≡ 10^{-6}

Complete details of the input data requirements, together with extensive comments on basic assumptions, usage, and ways to extend the simulation are given in the program listing in Appendix A. This program is written in FORTRAN IV to run on the IBM 360/50 level G compiler.

The naming of variables and parameters corresponds closely to the notation of the text and a complete listing is given in Table (5-2). For example, RDKL corresponds to the retention degradation of k_ℓ defined in Equation (IV-13). The program itself lists all essential names together with appropriate units[1] in its output.

The variables are stored in matrices U(I,J), U1(I,J), and U2(I,J) and their derivates in DF(I,J), DF1(I,J), and DF2(I,J) as defined in the listing. The bulk of the storage is in blank or labelled common in order to avoid unnecessary address transfers. The total storage is quite small, and is approximately thirty times the number of column slices considered (NSLICE). Since one seldom needs to consider more than 100 slices, the maximum requirements[2] are 3,000 units (12K bytes, since single precision is used). On a smaller computer, this storage requirement could be reduced by at least a factor of three if Stimberg's algorithm (STIMBERGCN)[3] were used, and the pressure profile was not saved.

The program achieves its CPU time objectives provided that the concentration profiles are not too sharp. If backwashing or regeneration is not called for more frequently than every ten time steps, the program can compute 40 grid points per second of CPU time. This means that for a wide range of parameters Model I can be applied to a 20 foot industrial column and integrated over a 100 day period in less than 10 minutes of IBM 360/50 CPU time, giving two decimals or better of accuracy.

If it is desired to study the filtration or adsorption equations separately, these phenomena can be uncoupled by specifying the unwanted input concentration to be zero. In this case, the simulation program will set the relevant scale factors, (N_1, N_2, N_3, or N_4) equal to zero,

---

[1]The program accepts data in commonly used units, and makes appropriate conversions for internal use.

[2]Not including the program itself.

[3]For description of this algorithm, see Ref. (V-1).

so that in effect, only the desired phenomenon is integrated. The effects of regeneration and backwashing can also be "turned off", simply by setting the control values CMAX, TREGEN, DPMAX, and TBA larger than their greatest possible value during the simulation.

TABLE 5-1

List of Subroutines of Simulation Programs

Code Name	Function
MOC	Solve plug flow equations by a third order method of cnaracteristics and prints concentration profiles
BWASH	Simulates the effect of backwashing on the first section of the column
REGEN	Remove the first section of the column and place a fresh section at the end
UZT	Characteristic of normal ordinary differential equations (5) for adsorption and filtration
ZO	Initialization along T = 0, and after each backwash, integration by a fourth order Runge-Kutta method with respect to z (called by MOC)
TO	Initialization at column inlet, z = 0 interpretation by a fourth order Runge-Kutta method with respect to T (called by MOC)
UZ	Special form of characteristic normal equations in C and Y needed along T = constant, (called by ZO)
UT	Special form of characteristics normal equations in Q and S needed along Z = 0 (called by TO)

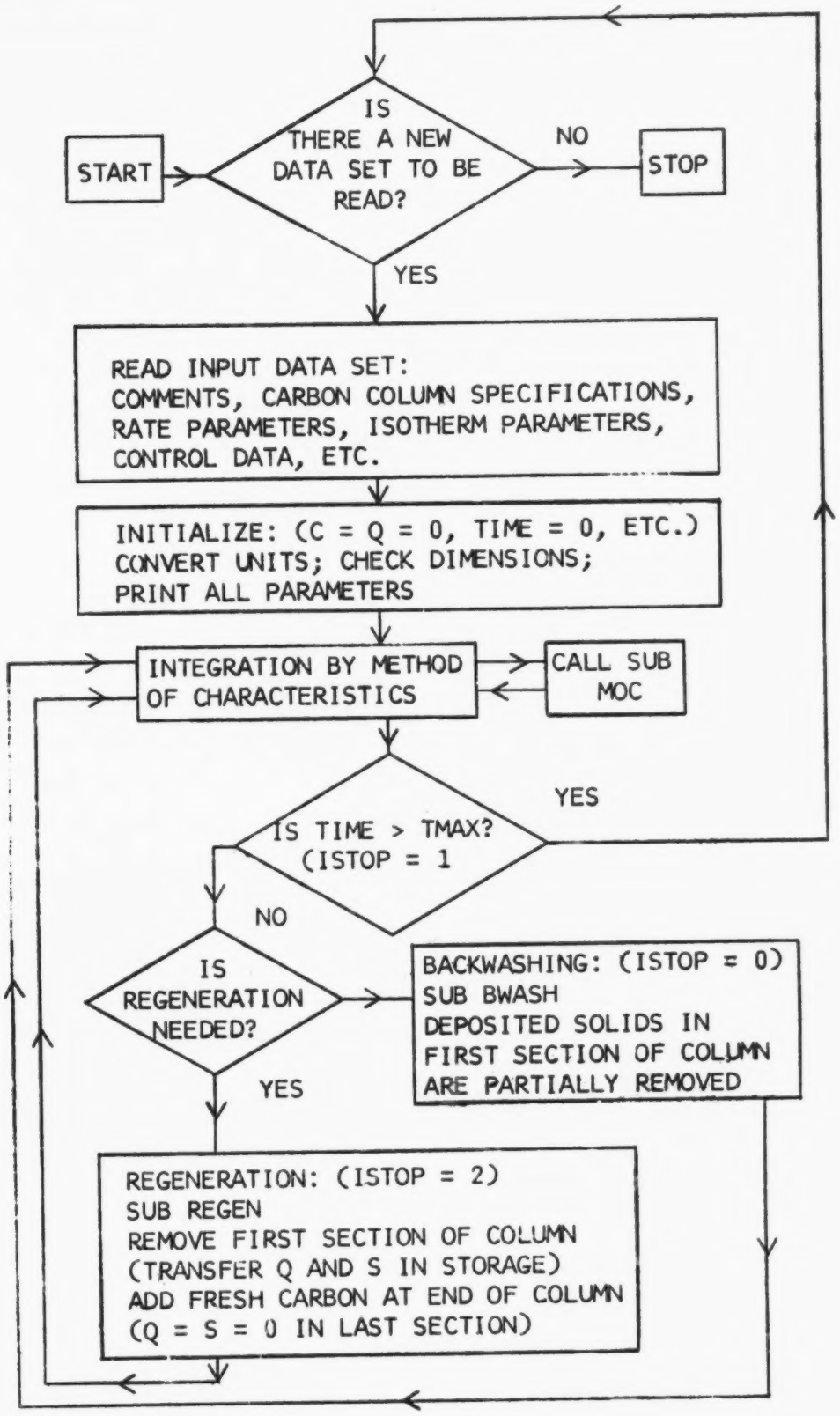

FIGURE (5-1) COMPUTER SIMULATION FLOW CHART: MAIN PROGRAM

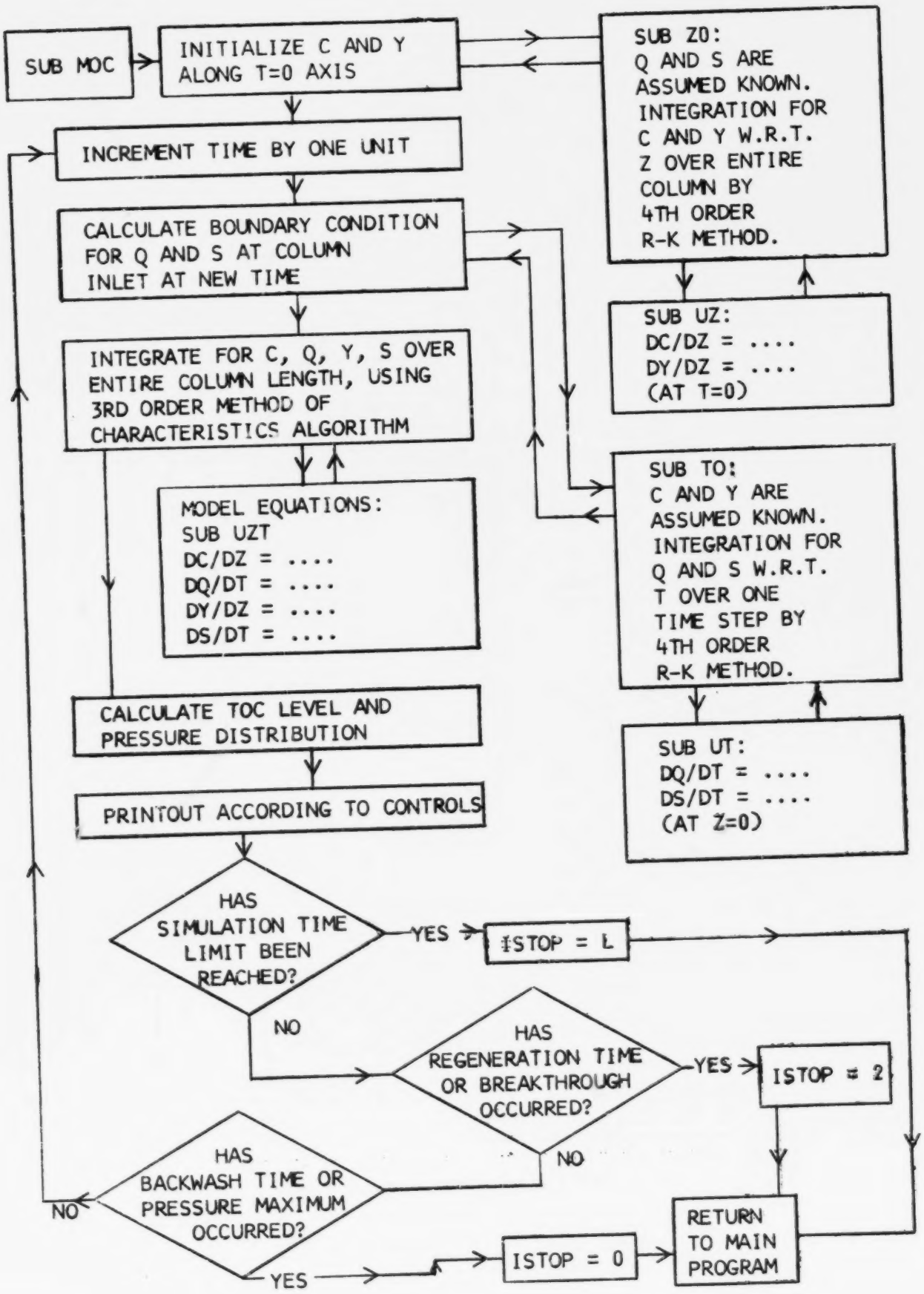
SUB MOC
INITIALIZE C AND Y ALONG T=0 AXIS
INCREMENT TIME BY ONE UNIT
CALCULATE BOUNDARY CONDITION FOR Q AND S AT COLUMN INLET AT NEW TIME
INTEGRATE FOR C, Q, Y, S OVER ENTIRE COLUMN LENGTH, USING 3RD ORDER METHOD OF CHARACTERISTICS ALGORITHM
MODEL EQUATIONS:
SUB UZT
DC/DZ = ...
DQ/DT = ...
DY/DZ = ...
DS/DT = ...
CALCULATE TOC LEVEL AND PRESSURE DISTRIBUTION
PRINTOUT ACCORDING TO CONTROLS
HAS SIMULATION TIME LIMIT BEEN REACHED?
YES
ISTOP = 1
NO
HAS REGENERATION TIME OR BREAKTHROUGH OCCURRED?
YES
ISTOP = 2
NO
HAS BACKWASH TIME OR PRESSURE MAXIMUM OCCURRED?
NO
YES
ISTOP = 0
RETURN TO MAIN PROGRAM
SUB Z0:
Q AND S ARE ASSUMED KNOWN.
INTEGRATION FOR C AND Y W.R.T. Z OVER ENTIRE COLUMN BY 4TH ORDER R-K METHOD.
SUB UZ:
DC/DZ = ...
DY/DZ = ...
(AT T=0)
SUB T0:
C AND Y ARE ASSUMED KNOWN.
INTEGRATION FOR Q AND S W.R.T. T OVER ONE TIME STEP BY 4TH ORDER R-K METHOD.
SUB UT:
DQ/DT = ...
DS/DT = ...
(AT Z=0)

FIGURE (5-2) COMPUTER SIMULATION FLOW CHART: CALCULATION SUBROUTINES

TABLE 5-2 List of Variables and Parameters

Physical Quantity	Nonconductive in Text	Computer Name
bulk density	p_B	PB
superficial velocity	u_o	UO
mean particle diameter	d_p	DP
void fraction of bed	ε_o	VOIDS
total length of column	L	L
number of sections	-	NS
dissolved TOC inlet concentration	c_o	CO
suspended solid inlet concentration	y_o	YO
suspended solid conversion factor for overall TOC values	-	SSCF
liquid film mass transfer coefficient for clear surfaces	k_{ℓ_o}	KLO
Freundlich isotherm parameters	b_1 and b_2	FI (1) and FI (2)
filtration coefficient	K_o	FC (1)
parameter relating σ with change of filtration coefficient	γ	FC (2)
retention degradation of liquid film mass transfer	r_d	RDKD
pressure gradient of fresh bed	$(\frac{\partial p}{\partial z})_o$	PRD (1)
parameter relating pressure drop increase with solid retention	γ	PRD (1)
slime residue factor after backwashing	-	SRF
time for backwashing	-	TBA

TABLE 5-2 List of Variables and Parameters (Cont'd.)

Physical Quantity	Nonconductive in Text	Computer Name
time for regeneration	-	TRENG
simulation interval	-	TMAX
maximum pressure drop	-	DPMAX
breakthrough concentration	-	CMAX
position increment	x_1	X (1)
time increment	x_2	X (2)
dimensionless parameter of governing equations	N_1 N_2 N_3 N_4	N (1) N (2) N (3) N (4)
solid phase transfer coefficient	k_s	KS

CHAPTER VI SIMULATION RESULTS

It shall be made clear at the outset that the results presented in this section are part of the verification of Model I. They are not intended for actual carbon column design, even though they can be utilized for that purpose under careful provisions. One should be cautioned that any design conclusions drawn from these tests must be tempered by the knowledge that hardly any physical parameters involved in this model have been satisfactorily determined. Considerable experimental work beyond those described in Parts II and III of this report is required. One simply cannot expect significant results from very approximate data.

As stated previously, the first objective of Model I is to indicate what experiments are urgently needed, and the second is to examine, by confrontation of adequate data, what modifications are required to improve the Model. The purpose of this work, therefore, is not merely a development of Model I which admittedly is a very crude model based upon available data at present, but the provision of a computation framework within a wide variety of models that can be examined without undue effort.

A number of the simulation tests were made with Model I to examine certain factors (such as increment size, magnitude of transfer coefficient, etc.). A summary of the conditions of these simulations are given in Table 6-1. The conclusion of these tests are given in the following:

(VI-A) Effect of Increment Size

A preliminary step in the utilization of the simulation program is the determination of increment sizes which are consistent with accuracy and computer time requirements. In practice, the accuracy of the simulation need not be appreciably greater than the accuracy of typical experimental data. Since TOC measurements have an associate uncertainty of at least ± 1 ppm, a computational error of ± 0.005 in the dimensionless concentration can generally be tolerated.

TABLE (6-1) MODEL INPUT PARAMETER IN SIMULATION TESTS

Text Notation	Computer Name	Units	Simulation Data Set Number (1)	(2)	(3)	(4)	(5)	(6)
ρ_B	PB	gm/cm^3	0.39	0.39	0.39	0.39	0.39	0.39
u_o	UO	gpm/ft^2	3.2	3.2	2.029	3.2	3.2	3.2
dp	DP	cm	0.0648	0.0648	0.0594	0.0648	0.0648	0.0648
ε	VOIDS	--	0.5	0.5	0.49	0.5	0.5	0.5
L	L	ft.	10.0	4.0	4.265	10.0	20.0	as shown
NS	NS	--	2	2	1	2	2	as shown
c_o	CO	gm/cm^3	0.28E-4	0.1E-4	0.0	0.28E-4	0.40E-4	0.40E-4
y_o	YO	--	0.0	0.5E-4	0.882E-4	0.0	0.10E-4	0.10E-4
SSCF	SSCF	gm/cm^3	1.0	1.0	1.0	1.0	1.0	1.0
D_s	DS	cm^2/sec	0.25E-10	0.25E-10	0.25E-10	as shown	0.40E-9	0.40E-9
k_{ℓ_o}	KLO	hr^{-1}	50.0	50.0	100	100.0	100	100
b_1	FI(1)	cm^6/gm^2	0.1354E 10	0.1354E 10	0.1345E 10	0.1354E 10	0.1354E 10	0.1354E 10
b_2	FI(2)	--	2.0	2.0	2.0	2.0	2.0	2.0
K_o	FC(1)	hr^{-1}	48.0	48.0	50.47	48.0	48.0	48.0
γ	FC(2)	--	67.0	67.0	30.46	67.0	67.0	67.0
n	FC(3)	--	2.5	2.5	5.095	2.5	2.5	2.5
r_d	RDKL	--	10.0	10.0	10.0	10.0	10.0	10.0
$(\partial P/\partial z)_o$	PRD(1)	atm/cm	0.15E-2	0.15E-2	0.3350E-3	0.15E-2	0.15E-2	0.15E-2
δ	PRD(2)	--	283.0	283.0	464.1	283.0	283.0	283.0
SRF	SRF	--	0.05	0.05	0.05	0.05	0.05	0.05

(Continued)

TABLE (6-1) MODEL INPUT PARAMETER IN SIMULATION TESTS (Cont'd.)

Text Notation	Computer Name	Units	Simulation Data Set Number (1)	(2)	(3)	(4)	(5)	(6)
TBA	TBA	hr.	320.0	320.0	48.0	320.0	96.0	96.0
TREGEN	TREGEN	hr.	200.0	200.0	200.0	200.0	2300.0	9000.0
TMAX	TMAX	hr.	120.0	64.0	20.0	120.0	2400.0	as shown
DPMAX	DPMAX	atm	4.0	4.0	1.0	4.0	10.0	3.0
CMAX	CMAX	gm/cm^3	0.30E-4	0.30E-4	1.0	0.30E-4	0.60E-4	as shown
x_1	X(1)	ft.	as shown	as shown	0.164	as shown	0.5	0.5
x_2	X(2)	hr.	as shown	as shown	0.250	as shown	4.0	2.0
N_1	N(1)	--	19.482	7.7927	0.0	--	77.927	62.341
N_2	N(2)	--	10.518	29.449	0.0	--	0.92028	0.92028
N_3	N(3)	--	0.0	7.4810	13.228	--	37.405	29.924
N_4	N(4)	--	0.0	7.4650	11.634	--	0.93312E-1	0.93312E-1
k_s	KS	hr^{-1}	0.3215E-3	0.3215E-3	0.3826E-3	--	0.5144E-2	0.5144E-2

There are two increments which have to be selected, a space step (x_1, in ft.) and a time step (x_2, in hr.). The effect of the increment size chosen on the accuracy of the calculations will vary according to the values of the physical parameters. In general, the more abrupt the concentration profiles are (implying relatively large values of D_s, k_ℓ , and K_o), the smaller the increments must be to attain a specified accuracy. A change in an exponent such as "n" in the filtration equations can have a pronounced effect on accuracy, and the general picture is complex because of the large number of parameters involved. Some specific criteria for Model I could be set up (in graphical form), but rather than this, a general procedure will be given for finding appropriate increments.

The starting point of this procedure is a nominal increment size which is thought to be adequate. If this is not available from previous simulation experiments, the values $x_1 = 0.5$ ft. and $x_2 = 1.0$ hr. may be used. A simulation sequence is then carried out on the computer in which the increment sizes are varied systematically. All parameters used in this test sequence should have their actual values, except for the simulation time (TMAX), which need not be more than 50 hours. Experience with Model I indicates that the largest errors occur in the initial period of simulation, and after this point the accuracy is remarkably well-maintained. It is not unusual for the accuracy to improve as saturation conditions are approached.

The increments x_1 and x_2 should be varied by several factors of two on either side of their nominal values. Thus, if the nominal increments are denoted by (0.5, 1), the simulation sequence might consist of nine runs as follows: (0.5, 1), (0.5, 2), (0.5, 4), (0.5, 0.5), (0.5, 0.25), (1, 1), (2, 1), (0.25, 1), (0.125, 1). If, on examining the results of this run sequence, it is found that the nominal increments were seriously in error, new values should be selected and a new run sequence carried out. The desired accuracy has been reached when the concentration variables at the same time and position in the column agree to the requisite number of decimal places.

An example of this procedure is given in Tables (6-2) and (6-3). Some of the batch experiments performed in this laboratory (see Part II) gave an average solid diffusion coefficient of 0.25E-10, and the corresponding isotherm and bed parameters are shown in Table (6-1) under simulation data set (1). The filtration effects were eliminated by setting $y_o = 0.0$, and the experiments in Table (6-2) were carried out starting from nominal increments of (0.5, 4). The results indicate that to obtain a consistency error of $\pm$ 0.00005 in C and Q the increments should be chosen so that $x_1 \leq 1$ ft. and $x_2 \leq 32$ hr. In this example, Q preserved a relative accuracy of four significant figures as well as the absolute accuracy stated above. No deterioration in accuracy is observed between z = 1 ft. and z = 10 ft. or between t = 32 hr. and t = 96 hr. To find increments for the filtration process, the parameters in data set (2) of Table (6-1) were employed. The adsorption phenomena were left operative, and the nominal pair of increments (0.5, 4) were chosen. The first experiments (omitted for brevity) showed that these nominal values were unsatisfactory, and a second sequence with nominal values (0.25, 1) is shown in Table (6-3). By comparing approximate Y and S values, it was found that for a consistency error $\leq \pm$ .0005, the increments should be chosen so that $x_1 \leq 0.125$ ft. and $x_2 \leq 1.0$ hr.

In these two examples, the filtration process is much more efficient than the adsorption process, and, consequently, requires smaller increments. When the two phenomena are coupled, it is generally necessary to base the increment size on the more sensitive set of equations. However, since the effective TOC carried by the suspended solids is considerably less than that carried by dissolved substances, a somewhat larger error can be accepted in the filtration equations provided that the adsorption equations are not significantly "contaminated". For Model I, the question of stability is subordinate to the question of accuracy, because in all experiments carried out, adequate accuracy ensured stability. The filtration equations in the example above will become unstable and"blow up" if $x_2 \geq 16$ hr., but this is well outside of the accuracy range found desirable. Mild oscillations can sometimes be tolerated, as, for example, in the effluent of a long column over the first 24 hours of operation. It has been found that such oscillations

TABLE (6-2) TEST ON INCREMENT SIZE (Adsorption Increments) Data Set (1)

Expt. No.	x_1 ft.	x_2 hr.	C(32,1)	C(32,10)	C(96,1)	C(96,10)
1	0.5	2.0	0.864357E 0	0.376708E 0	0.866435E 0	0.381179E 0
2	0.5	4.0	0.864357E 0	0.376707E 0	0.866433E 0	0.381174E 0
3	0.5	8.0	0.864356E 0	0.376706E 0	0.866432E 0	0.381172E 0
4	0.5	32.0	0.864353E 0	0.376685E 0	0.866428E 0	0.381152E 0
5	0.25	4.0	0.864358E 0	0.376706E 0	0.866433E 0	0.381175E 0
6	1.0	4.0	0.864341E 0	0.376693E 0	0.866383E 0	0.381163E 0
7	2.0	4.0	--	0.376450E 0	--	0.380971E 0
			Q(32,1)	Q(32,10)	Q(96,1)	Q(96,10)
1	0.5	2.0	0.659755E-2	0.134955E-2	0.196619E-1	0.405690E-2
2	0.5	4.0	0.659755E-2	0.134956E-2	0.196619E-1	0.405689E-2
3	0.5	8.0	0.659756E-2	0.134954E-2	0.196619E-1	0.405686E-2
4	0.5	32.0	0.657341E-2	0.132665E-2	0.196383E-1	0.403432E-2
5	0.25	4.0	0.659757E-2	0.134955E-2	0.196620E-1	0.405688E-2
6	1.0	4.0	0.659747E-2	0.134945E-2	0.196609E-1	0.405660E-2
7	2.0	4.0	--	0.134773E-2	--	0.405187E-2

Result: for consistency to ± .00005, $x_1 \leq 1$ ft.

$x_2 \leq 32$ hrs.

TABLE (6-3) TEST ON INCREMENT SIZE (Filtration Increments) Run Sequence (2)

Expt. No.	x_1 ft.	x_2 hr.	Y(16,1)	Y(16,4)	Y(64,1)	Y(64,4)
1	0.25	4.0	0.638348E 0	0.130144E-1	0.853640E 0	0.321359E 0
2	0.25	2.0	0.634081E 0	0.131668E-1	0.852676E 0	0.320606E 0
3	0.25	1.0	0.632232E 0	0.132184E-1	0.852278E 0	0.320249E 0
4	0.25	0.5	0.631635E 0	0.132211E-1	0.852129E 0	0.320069E 0
5	0.5	2.0	0.657553E 0	0.895232E-2	0.858748E 0	0.333212E 0
6	0.125	1.0	0.630680E 0	0.135576E-1	0.851834E 0	0.319415E 0
7	0.0625	1.0	0.630560E 0	0.135906E-1	-- *	-- *
			S(16,0)	S(16,4)	S(64,0)	S(64,4)
1	0.25	4.0	0.128046E-1	0.163895E-3	0.262944E-1	0.861945E-2
2	0.25	2.0	0.133695E-1	0.176115E-3	0.266366E-1	0.862130E-2
3	0.25	1.0	0.136372E-1	0.180617E-3	0.268001E-1	0.861826E-2
4	0.25	0.5	0.137671E-1	0.181561E-3	0.268797E-1	0.861475E-2
5	0.5	2.0	0.133695E-1	0.989664E-4	0.266366E-1	0.888225E-2
6	0.125	1.0	0.136372E-1	0.186690E-3	0.268001E-1	0.860659E-2
7	0.0625	1.0	0.136372E-1	0.187173E-3	-- *	-- *

* Computer run terminated inadvertently

Result: for consistency to ± .0005, $x_1 \leq 0.125$ ft.

$x_2 \leq 1.0$ hr.

are damped out, and do not significantly affect the results of long simulations. Similarly, if most of the filtration is taking place near the column inlet, it may happen that the retention (S) becomes negative (and very small) near the bottom of the column. This indicates that the increments are too large, but it can sometimes be tolerated. One condition that cannot be allowed is an oscillation near the column inlet. If, for example, the second value of C or Y is lower than the third value, then the space increment must be decreased.

(VI-B) Comparison with Filtration Results

As a test of the integration scheme and also of the filtration equations in Model I, a run was made to simulate the calculated results as reported in Part III of this report. These results pertain to a column length 130 cm, with an integration point every 5 cm. Due to the special form of the filtration equations in Model I, they can be uncoupled and integrated independently of each other. One integration is carried out (analytically) for S at the column inlet, and then a second differential equation with Z as the independent variable is solved with the Adams-Moulton predictor-corrector algorithm to find Y at equally spaced points in the column. The parameters used are shown in Table (6-1) as data set (3), and the compared results are shown in Table (6-4). The results reported in Part IV may be regarded as accurate to five significant figures. However, the parameters used are known only to four significant figures, so perfect agreement is not possible. The actual results agree to three or four decimals, with the largest discrepany in Y being 0.005 at z = 10 cm, t = 1 hr. Reductions in increment size would doubtless improve the agreement, but only up to a certain point. The pressure profiles from [M-3] cannot be readily compared with the simulation output, because in the experimental work the value of δ in Equation (IV-11) was calculated using trapezoidal integration. This is not adequate for dealing with sharp S-profiles, and causes discrepancies of 10% to 20% when compared with the Simpson's rule integration of the simulation program.

TABLE (6-4) COMPARISON WITH FILTRATION RESULTS

z cm	T = 1.0 hr.				T = 6.0 hr.			
	Y_p^1	Y	σ_p^1	S	Y_p	Y	σ_p	S
0.00	1.000	1.000	0.3410E-2	0.3297E-2	1.000	1.000	0.1117E-1	0.1104E-1
10.00	0.495	0.500	0.1687E-2	0.1698E-2	0.765	0.766	0.8543E-2	0.8568E-2
20.00	0.210	0.213	0.7176E-3	0.7222E-3	0.527	0.529	0.5888E-2	0.5919E-2
30.00	0.082	0.082	0.2784E-3	0.2782E-3	0.313	0.315	0.3498E-2	0.3519E-2
40.00	0.030	0.030	0.1034E-3	0.1023E-3	0.156	0.157	0.1742E-2	0.1744E-2
50.00	0.011	0.011	0.3773E-4	0.3689E-4	0.067	0.066	0.7449E-3	0.7349E-3
60.00	0.004	0.004	0.1368E-4	0.1321E-4	0.026	0.025	0.2897E-3	0.2795E-3
70.00	0.001	0.001	0.4950E-5	0.4723E-5	0.010	0.009	0.1077E-3	0.1013E-3
80.00	0.001	0.000	0.1790E-5	0.1687E-5	0.004	0.003	0.3933E-4	0.3603E-4
100.00	0.000	0.000	0.2338E-6	0.2154E-6	0.000	0.000	0.5162E-5	0.4484E-5
120.00	0.000	0.000	0.3052E-7	0.2753E-7	0.000	0.000	0.6745E-6	0.5558E-6
		T = 9.5 hr.				T = 16 hr.		
0.00	1.000	1.000	0.1412E-1	0.1401E-1	1.000	1.000	0.1792E-1	0.1783E-1
10.00	0.828	0.829	0.1170E-1	0.1172E-1	0.884	0.885	0.1585E-1	0.1586E-1
20.00	0.644	0.646	0.9100E-2	0.9129E-2	0.758	0.759	0.1358E-1	0.1360E-1
30.00	0.455	0.457	0.6432E-2	0.6459E-2	0.620	0.621	0.1111E-1	0.1114E-1
40.00	0.280	0.282	0.3955E-2	0.3968E-2	0.473	0.475	0.8484E-2	0.8505E-2
50.00	0.145	0.145	0.2044E-2	0.2038E-2	0.325	0.327	0.5831E-2	0.5841E-2
60.00	0.064	0.063	0.8982E-3	0.8813E-3	0.193	0.194	0.3451E-2	0.3445E-2
70.00	0.025	0.024	0.3546E-3	0.3394E-3	0.096	0.096	0.1713E-2	0.1691E-2
80.00	0.009	0.009	0.1327E-3	0.1235E-3	0.041	0.040	0.7302E-3	0.7059E-3
100.00	0.001	0.001	0.1763E-4	0.1546E-4	0.006	0.005	0.1054E-3	0.9600E-4
120.00	0.000	0.000	0.2308E-5	0.1906E-5	0.001	0.000	0.1395E-4	0.1193E-4

[1]The variables subscripted "p" are Payatakes' results.

(VI-C) Effect of Solid Diffusion and Liquid-Phase Mass Transfer on Adsorption

Having found suitable increment sizes for integration, Model I was used to examine the effect of D_s and k_ℓ. It has been suggested [W-4] that adsorption in packed columns might be controlled by the liquid-side mass transfer resistance during the brief period after startup ($T \approx 0$). Under the assumption of zero solid-side resistance ($Q = Q^*$, $k_s \to \infty$), it can be shown that for the Freundlich isotherm

$$q^* = b_1 c^{*\,b_2} \tag{VI-1}$$

and no interaction effects ($r_d = 0$), the adsorption equations in Model I (5.45, 5.46) become

$$\frac{dC}{dZ} = -\left(\frac{k_\ell L}{u_o}\right)\left(C - Q^{1/b_2}\right) \tag{VI-2}$$

$$\frac{dQ}{dT} = \left(\frac{c_o^{\,b_2-1}}{\rho_B b_1}\right)\left(C - Q^{1/b_2}\right) \tag{VI-3}$$

The initial profile would thus be

$$C = c/c_o = -\left(k_\ell L/u_o\right) \exp\left(z/L\right) \tag{VI-4}$$

Using Equation (VI-4) and some preliminary data of Hsieh* for five foot columns, k_ℓ was estimated as 4.7 hr^{-1} which is at least two orders of magnitude lower than that estimated from Equation (IV-5). This larger discrepancy can be readily explained as a pre-treatment effect. The waste water used in Hsieh's work had not been coagulated with aluminum and was visibly polluted with cloudy colloid suspension. The rather fast coating of these colloidal matters onto the carbon surface undoubtedly increases the resistance to mass transfer and results in a much lower value of k_ℓ.

Simulation runs were made with the calculated value of k_ℓ used as k_ℓ and the solid diffusion coefficient mentioned in Section (IV-B). It was found

*Unpublished Data, Department of Chemical Engineering and Metallurgy, Syracuse University

a) that the calculated effluent from 10 ft. and 20 ft. columns was considerably higher than reported from the industrial pilot plants [E-1], and

b) that the liquid-side mass transfer coefficient as calculated was not the controlling resistance (k_{ℓ_o} could be 100 times as large without appreciably affecting the effluent TOC concentration).

The effect of the solid diffusion coefficient D_s was explored using the simulation data set (4) in Table (6-1). Concentration profiles for C are shown in Figure (6-1). Increasing values of D_s make the C-profiles increasingly sharp, but above $D_s = 1.6 \times 10^{-9}$ cm^2/sec the liquid film resistance ($k_{\ell_o} = 100\ hr^{-1}$) becomes limiting. Figure (6-2) shows the corresponding solid-phase Q-profiles. As D_s increases, it is necessary to decrease the integration increments. The time-step x_2 must be varied inversely with D_s, while the space-step x_1 remains fairly constant. This behavior is entirely expected since D_s (or k_s) is used to scale the time variable.

Taking $D_s = 0.4 \times 10^{-9}$ as a starting point, the liquid-phase mass transfer coefficient was decreased to determine its effect. The results are shown in Figure (6-3). The curves for $k_{\ell_o} = 100$ and $k_{\ell_o} = 20$ are indistinguishable, but for $k_{\ell_o} = 10$ the liquid side resistance is clearly the controlling one. Lower values of k_{ℓ_o} inhibit the overall adsorption almost entirely.

(VI-D) Adsorption and Filtration Profiles Over a Hundred-Day Period

The combined effects of filtration and adsorption were simulated over a hundred-day period with the parameters in data set (5) of Table (6-1). The concentration and pressure profiles for the first ten feet are shown in Figures (6-4), (6-5), (6-6), (6-7), and (6-8) at four times. The adsorption curves for C and Q are shown at intervals of about 33 days. Regular backwashing of the first half of the column occurs every four days, but no regeneration is allowed. If an adsorption zone is defined by some arbitrary concentration range such as $0.2 \leq C \leq 0.5$, it can be observed from Figure (6-4) that this zone expands in a nonlinear manner as it moves down the column. At 24 hours this zone is only 1.2 ft. long,

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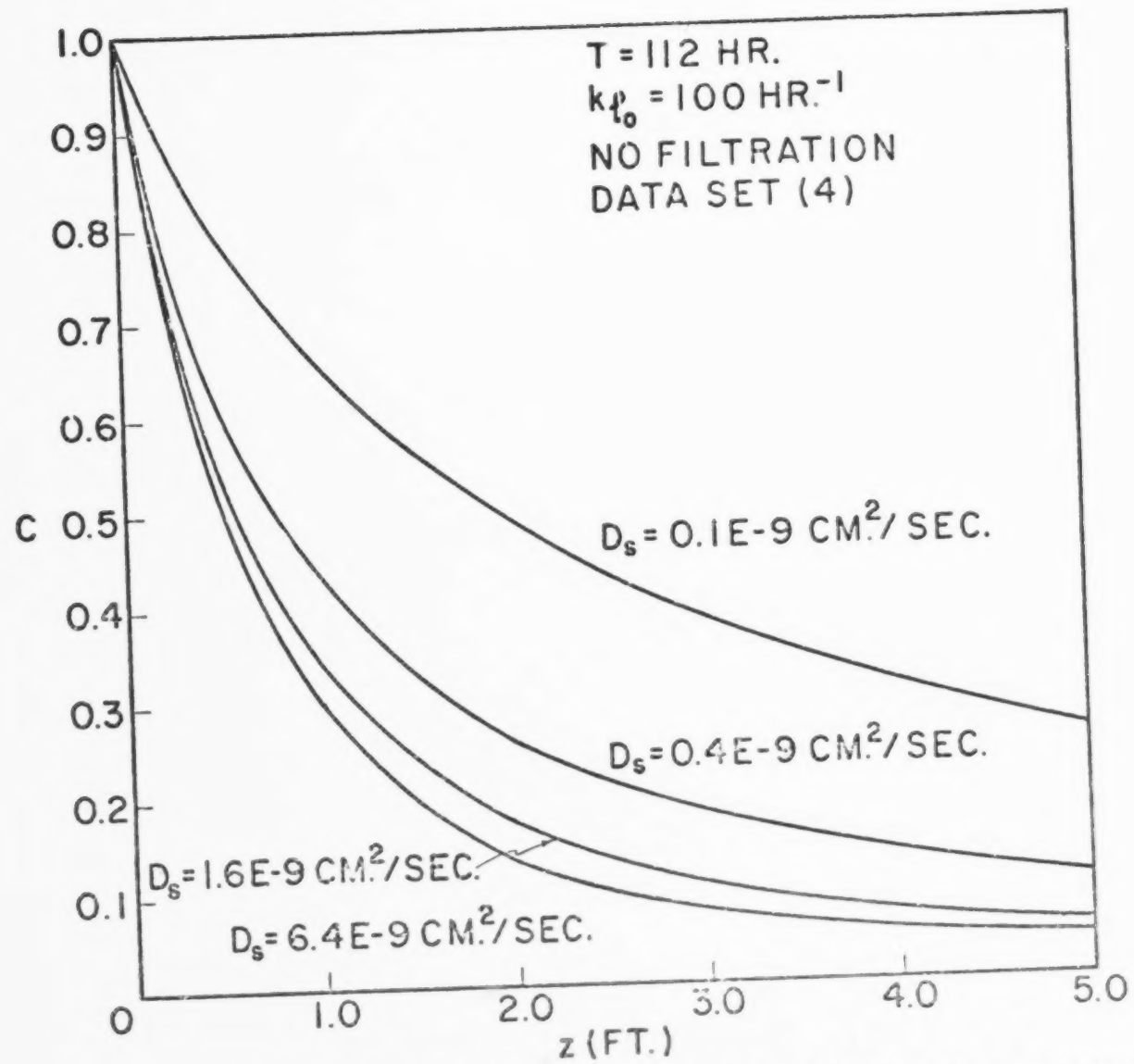

FIG. (6-1) EFFECT OF SOLID DIFFUSION COEFFICIENT ON C

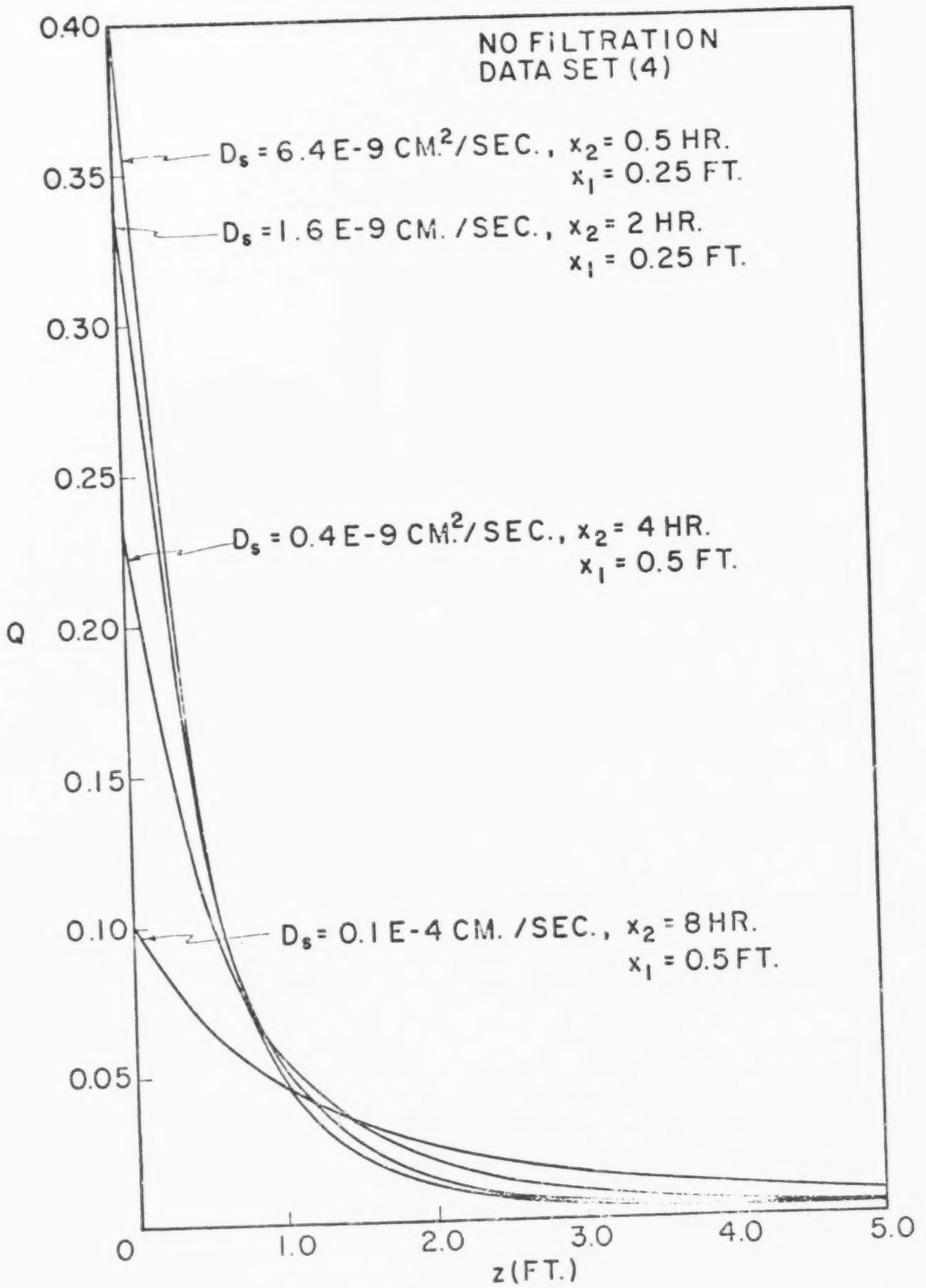

FIG. (6-2) EFFECT OF SOLID DIFFUSION COEFFICIENT ON Q

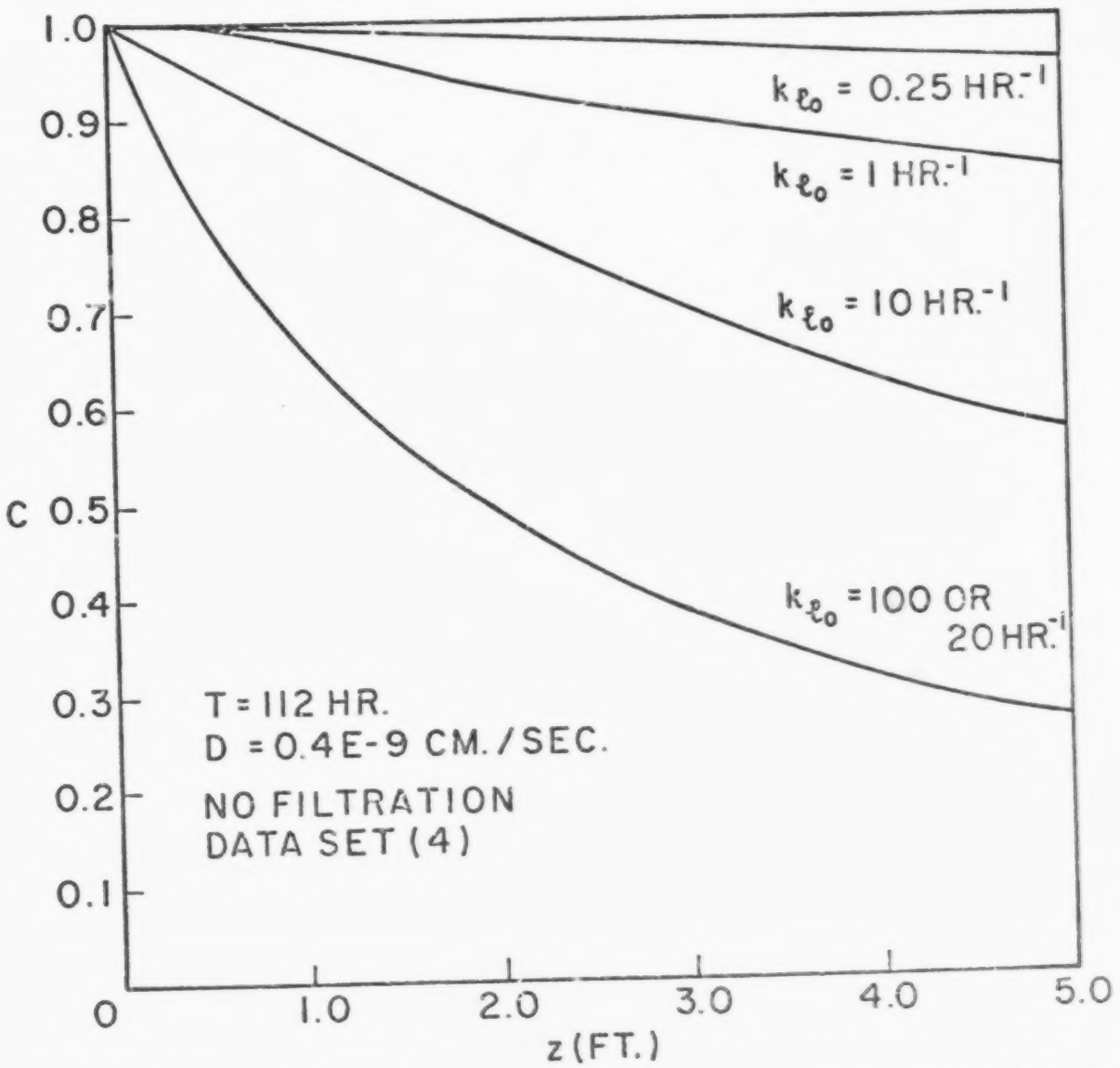

FIG. (6-3) EFFECT OF LIQUID-PHASE MASS TRANSFER COEFFICIENT ON C

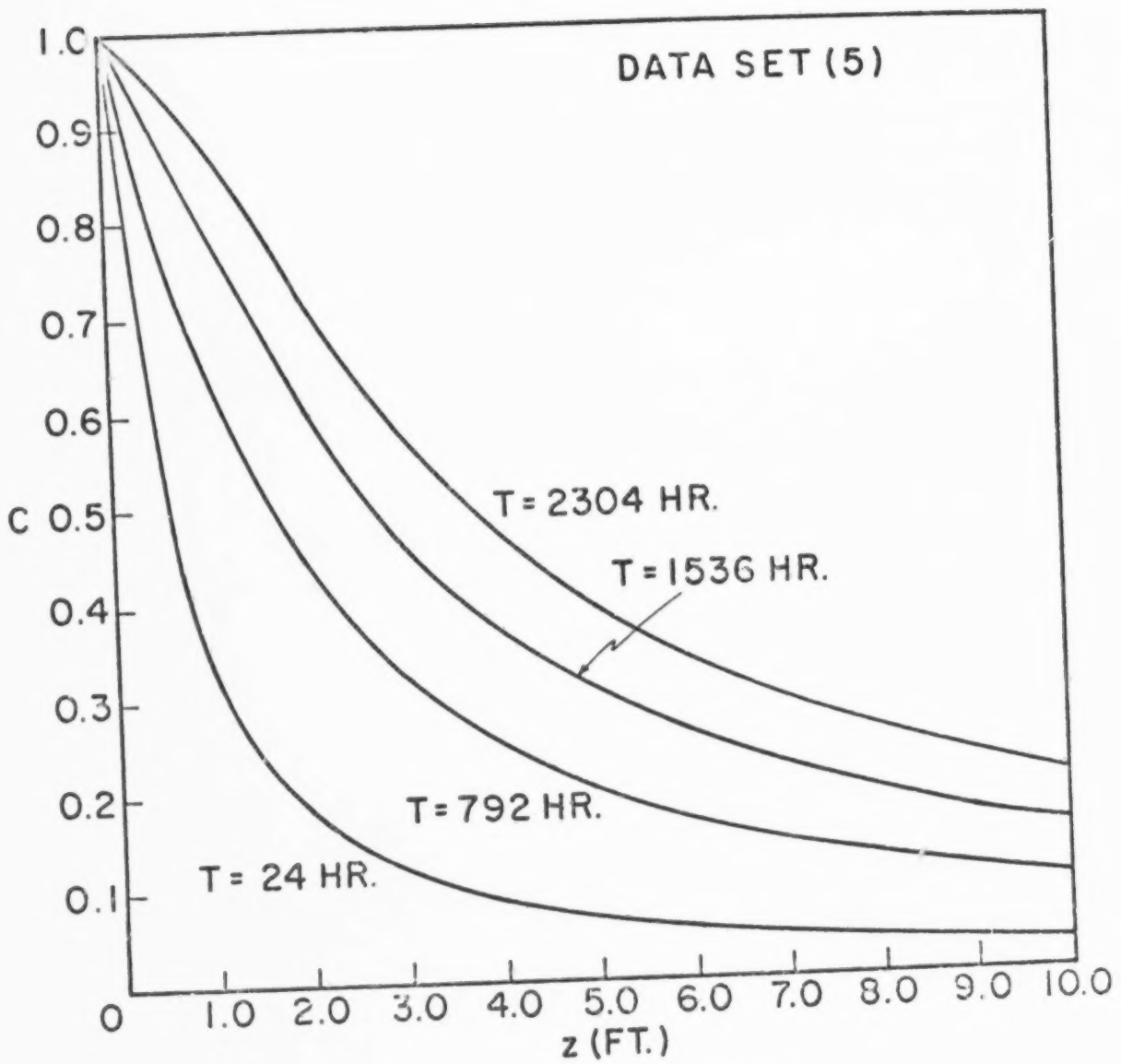

FIG. (6-4) C-PROFILES OVER 100 DAYS

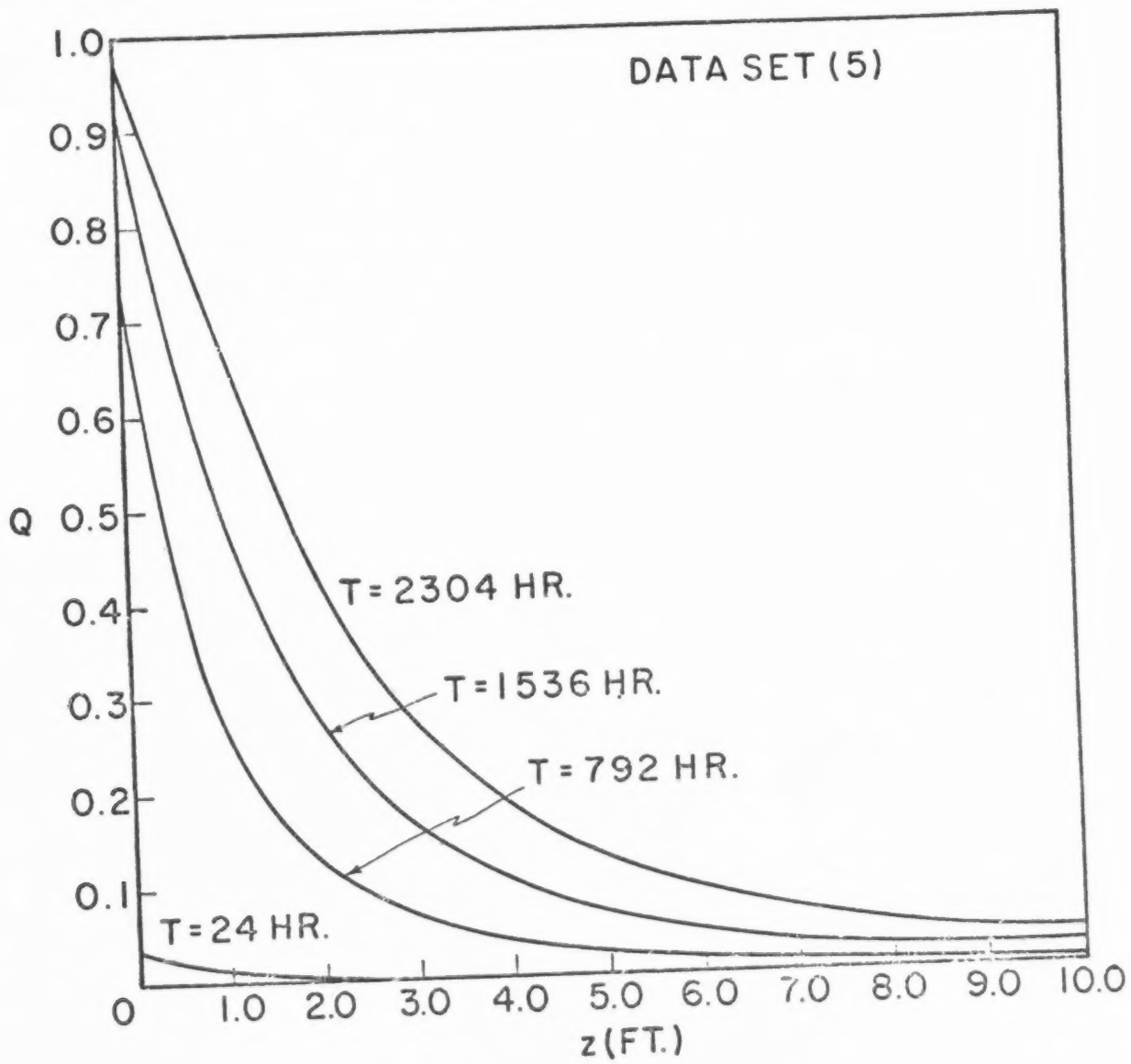

FIG. (6-5) Q-PROFILES OVER 100 DAYS

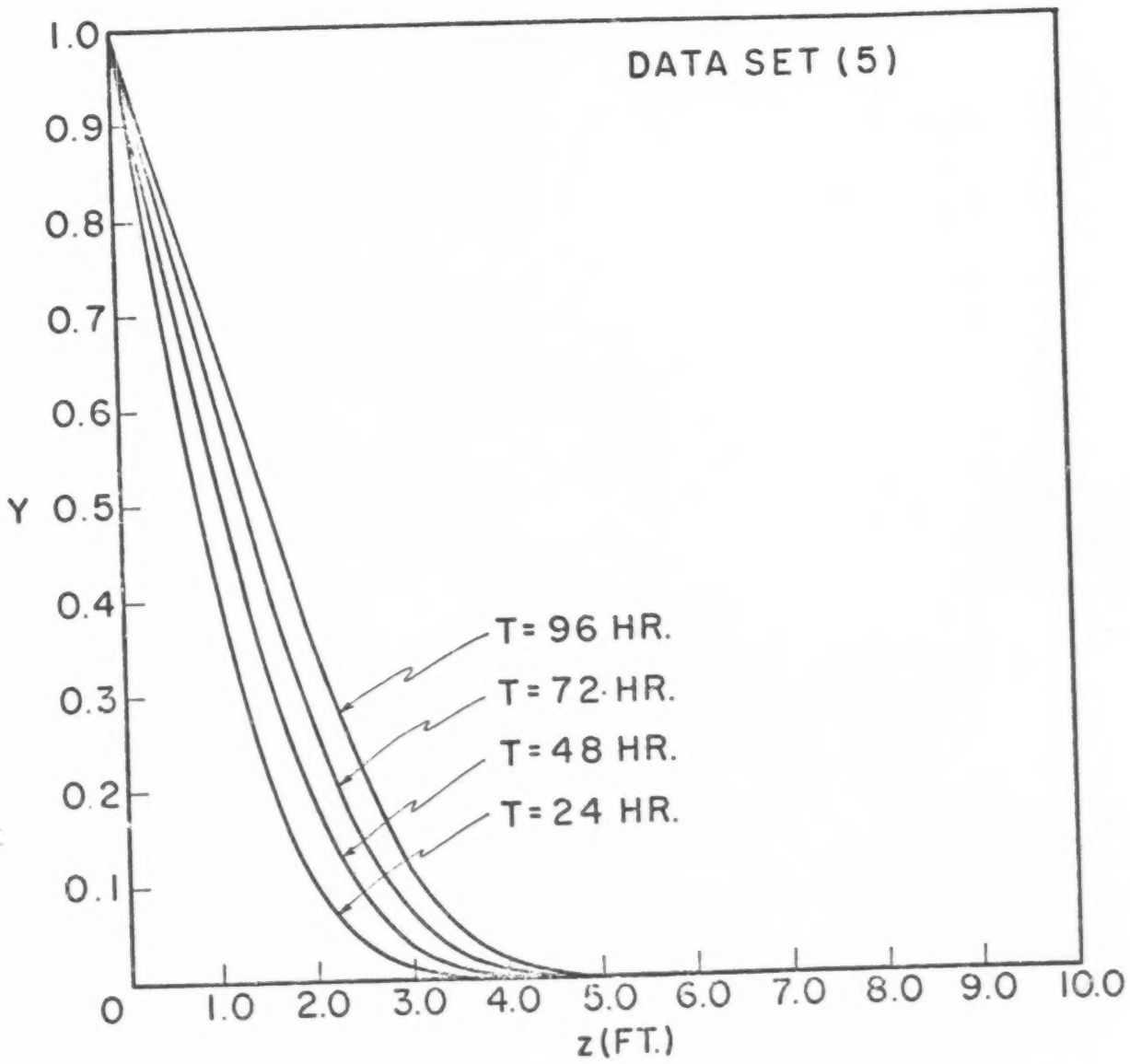

FIG. (6-6) Y-PROFILES OVER 4 DAYS

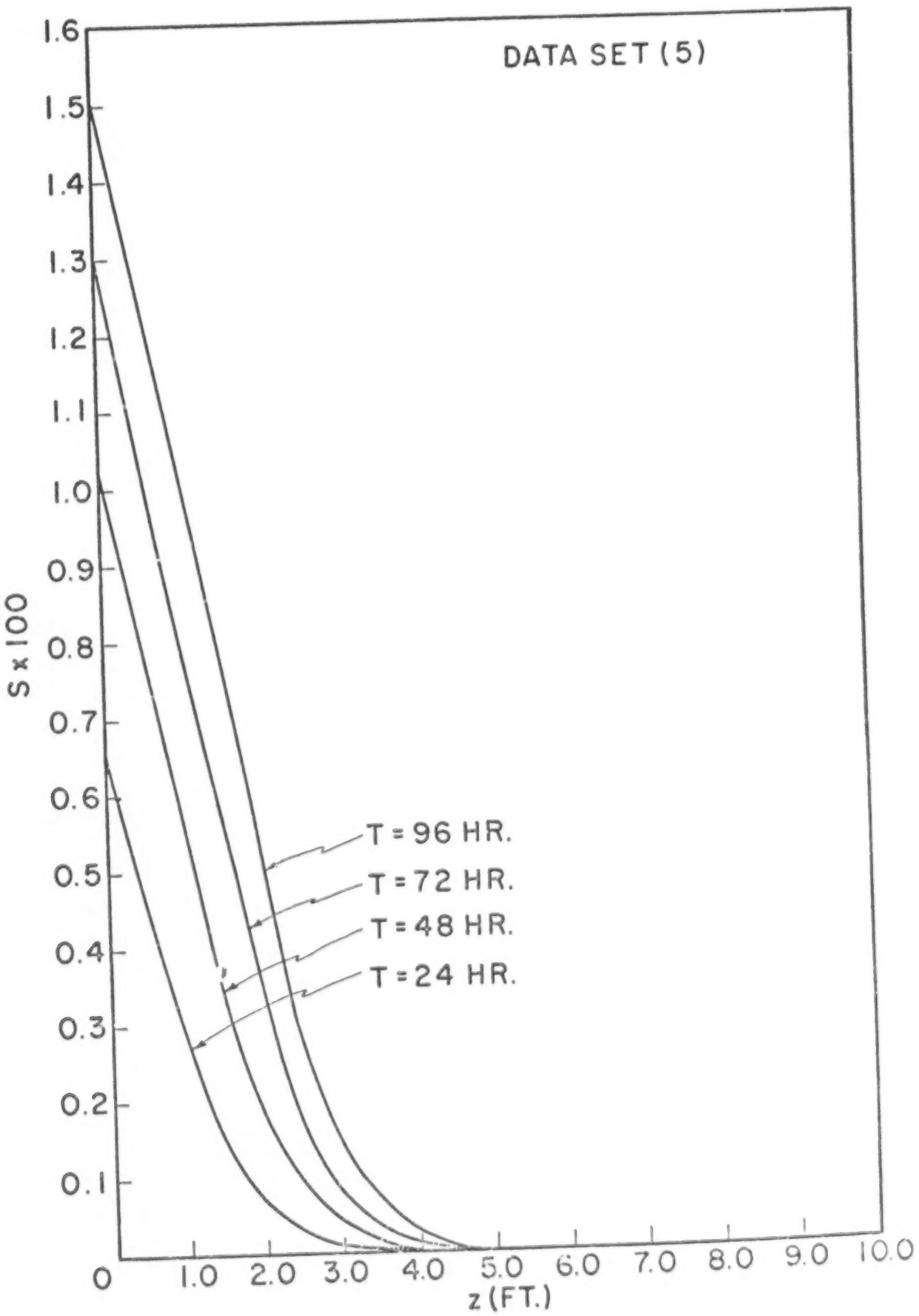

FIG. (6-7) S-PROFILES OVER 4 DAYS

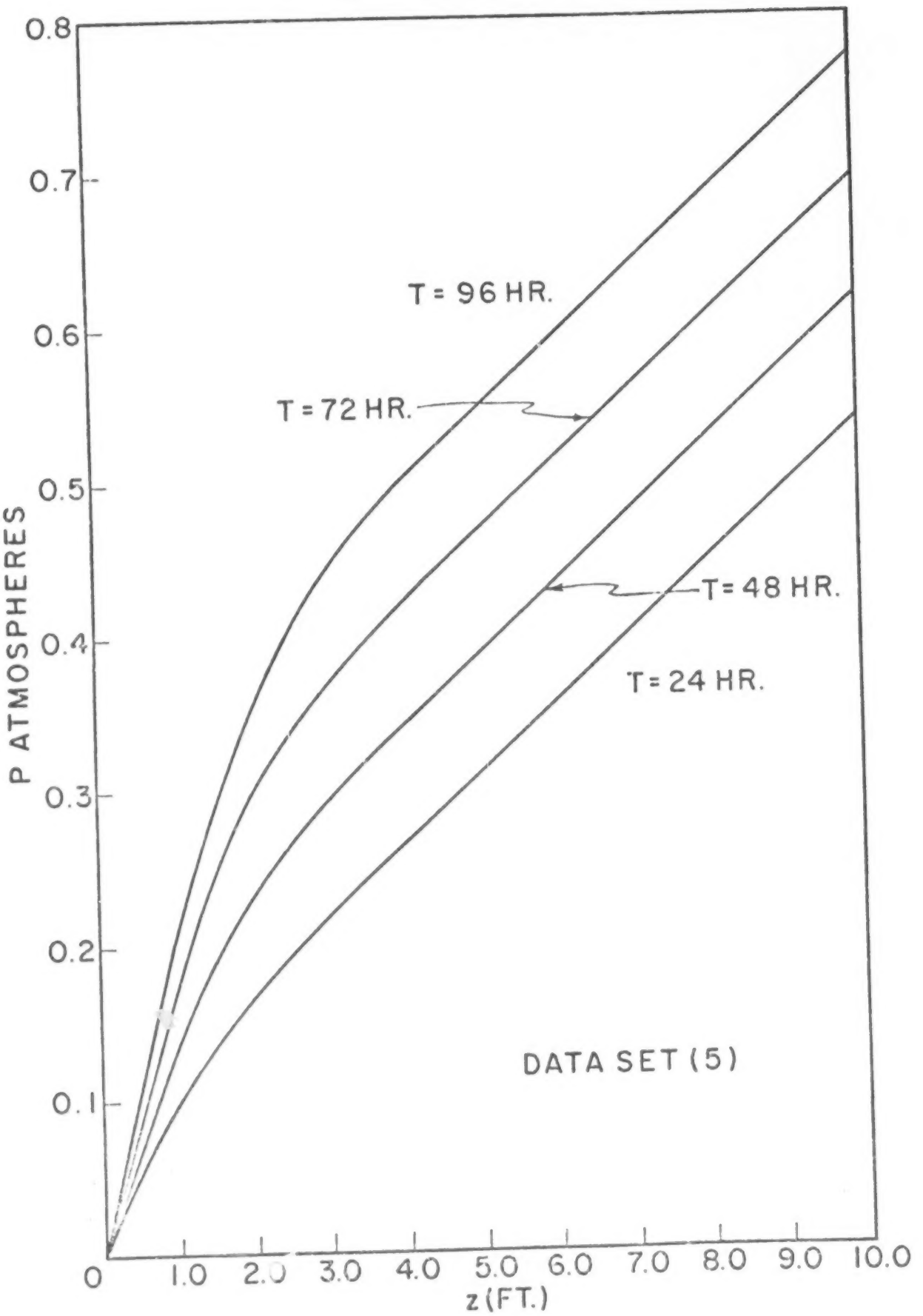

FIG. (6-8) P-PROFILES OVER 4 DAYS

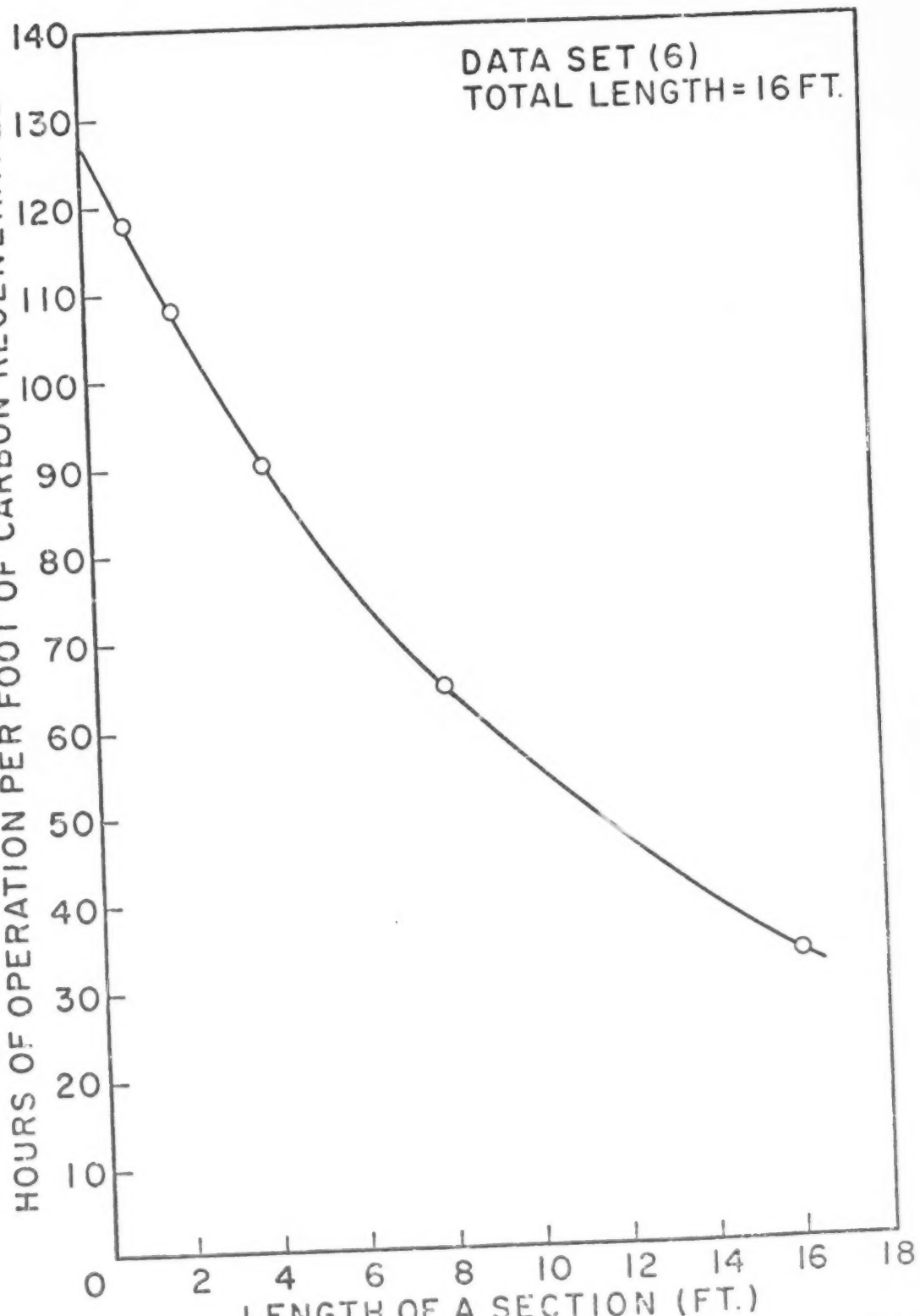

FIG. (6-9) VARIATION OF COLUMN PERFORMANCE WITH NUMBER OF SECTIONS

but at 2304 hours it is 6.5 ft. long. The rear end of this zone moves at an even pace down the column, but the front end accelerates. This behavior agrees with the findings of English [E-1] for waste water in carbon columns, and Vermeulen's predictions for unfavorable isotherms [V-1].

The filtration and pressure profiles have been recorded for the first backwash cycle only. Due to the simplicity of the backwash model, the backwash cycles become completely regular after 384 hours as shown below in Table (6-5):

TABLE (6-5) BACKWASH CYLES

Cycle No.	Time hr	S(T,0)	P(T,20) atm
1	96	0.015095	1.2324
2	192	0.015247	1.2483
3	288	0.015249	1.2491
4	384	0.015249	1.2492
5	480	0.015249	1.2492

The filtration parameters used throughout this chapter have been taken from Payatakes' and Mehter's* experiments with activated carbon/clay suspensions. Real waste water may behave somewhat differently.

(VI-E) Effect of Regeneration and Number of Sections Over Extended Periods

As an example of the sort of question that the simulation can be used to answer, it was desired to investigate the relationship between column length and quantity of carbon to be regenerated per unit time. This point is important, because the capital costs required to build waste water treatment plants are much greater than the operational costs. If a 10 foot carbon column could be used instead of a 20 or 30 foot column, considerable additional regeneration might be feasible for an overall lower cost.

The parameters in data set (6) of Table (6-1) were used to compare a 10 foot column and a 20 foot column. Both columns had two sections, and the breakthrough concentration was set at 3 ppm TOC. Operation was

*See Part III of this Report

simulated over a year, and both columns came to a pseudo-steady state of operation after a few cycles. The larger column required the regeneration of 10 ft. of carbon every 1252 hr., while the smaller column required the regeneration of 5 ft. of carbon every 444 hr. The smaller column thus has a regeneration rate which is 43% higher than the larger column.

To see if this result depends on the breakthrough level chosen, the maximum allowable concentration was reduced to 2 ppm, and the same two columns were simulated over a half year period. This time, the larger column required regeneration every 742 hr., and the smaller column every 192 hr. This shows that under the tighter effluent restrictions the smaller column needs a 93% higher regeneration rate than the larger column.

As another example, the effect of the number of sections was investigated. It is intuitively obvious that an infinite number of sections (continuous regeneration) will make the most efficient use of the carbon. Since this arrangement is probably impractical, it is necessary to know the relative efficiencies of 2 sections or 4 sections or 8 sections (note that the total length of column is assumed to be constant). The parameters in run sequence (6) were again used, but this time with a 16 ft. column over a three-month period.* The column was first simulated with one section, then with two, then with four, then with eight, and finally with sixteen sections. The results are shown in Table (6-6).

TABLE (6-6) EFFECT OF NUMBER OF SECTIONS

No. of Sections	Length of each Section (ft)	Time between Regenerations (hr)	Hr. of Operation per ft. Carbon Regenerated
1	16	578	33.0
2	8	518	64.75
4	4	360	90.0
8	2	216	108.0
16	1	118	118.0

The hours of operation per foot of carbon regenerated are plotted in Figure (6-9) against the length of a section. An extrapolation to zero

*CMAX = 2 ppm

length gives 128 hours per foot of carbon regenerated, which can be taken as the column's most efficient performance for this set of parameters. This performance can be alternatively expressed as 1010 gallons of waste water treated per pound of fresh carbon.

CHAPTER VII

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

(VII-A) Usage of the Simulation Program with Model I

It has been shown that Model I simulates the behavior of a carbon column in a reasonable manner. The results are qualitative rather than quantitative, however, and certain requirements must be met before Model I can be used for design. These requirements are:

(a) The filtration and pressure drop parameters must be determined experimentally for waste water suspensions rather than clay.

(b) The waste water used in these tests should be standardized in some way. The most important consideration is that of coagulation. It appears that most advanced waste water treatment systems of the future will include coagulation with lime or alum followed by sedimentation of mixed-media filtration prior to carbon adsorption. Laboratory and pilot plant studies should thus be based on a clarified primary or secondary effluent.

(c) Further rate and equilibrium studies are needed for the adsorption of TOC from clarified waste water. The simulation studies have already shown that 0.25 E-10 is too small a value for the solid diffusion coefficient (a more reasonable value would be D_s = 0.4 E-9).

(d) Experiments are needed to determine the suspended solids conversion factor (SSCF) for typical "clarified" waste water. One possible technique would be to take TOC and turbidimeter readings for unfiltered waste water samples, and repeat the measurements on samples which have been passed through a millipore filter. The turbidimeter reading may be related to the volumetric suspended solids concentration, and the difference between the TOC readings is due to the filterable solids.

(e) A better estimate is needed for RDKL, but this is difficult to obtain directly. Experiments on partially clogged beds with large pressure gradients might be useful, but the

parameter-fitting technique of section (VII-C) may be necessary.

(f) For lengthy simulations the adsorption parameters probably do not change much, but the same may not be true of filtration. If the detailed effects of backwashing cannot be readily discovered, then at least the filtration and pressure drop parameters must be based on beds which have been used and backwashed several times.

With some assurance on these points, Model I could become a powerful tool for laboratory, pilot plant, and full-scale design studies. The first of these has already been demonstrated; Model I has suggested critical new experiments, checked the magnitude of certain rate parameters and permitted the testing of simple backwash and regeneration effects. Pilot plants and actual sewage treatment facilities can be simulated before being constructed to estimate the length of carbon column needed for given effluent purity, the frequency of backwashing and regeneration, and the size of pump required to overcome the head loss. The effect of flow rate, number of sections, carbon and waste water properties can all be conveniently explored.

Model I, however, assumes no major biological effects. If such effects occur, Model I should still provide a basis for further calculations. A particular installation may pre-chlorinate its waste water and attempt to use carbon column adsorption without biological interference. In this case, a comparison of Model I simulations with actual plant data might reveal abnormal conditions at an early stage. Waste water facilities are often quite automated and unattended. A simulation program such as Model I could monitor periodically sampled data and test the plant performance. If the waste water quality changes appreciably (seasonal changes are quite large), then some of the parameters for the simulation must be reevaluated. This can either be done experimentally or by adding parameter-fitting techniques to the simulation. Further uses of the simulation technique are mentioned in the following sections.

(VII-B) Short-Term Improvements for Model I

The need for certain critical experimental data in Model I has already been discussed. There are several other desirable changes which might be made to Model I, and most of these have programming implications.

(a) Some of the rate parameters could be evaluated as functions of flow rate, carbon granule properties, and waste water properties. Equation (IV-5) has already been recommended for the estimation of k_{ℓ}, and similar equations can probably be found for the filtration effects. The smaller the number of parameters that must be specified, the easier it is to use the simulation.

(b) Since pilot plants never maintain a steady input concentration, the computer program for Model I should be able to accept time-varying values of c_o and y_o. One method for doing this would be to read in the information at the start of the simulation in triplets (c_o, y_o, t). An interpolation subroutine, (probably linear), could then be used to give inlet concentrations at any desired time; this would be called by subroutines UT and TO.

(c) The solid-side mass transfer can probably be better represented by Vermeulen's quadratic driving force expression, as already mentioned in section (IV-B). This requires reformulation of the model equations (the result should be called Model II), and will undoubtedly require longer CPU times.

(d) The computer running times can be appreciably improved by compiling the program on the FORTRAN IV level H compiler (with OPT = 2) and making an object deck. Present compilation times on the G level compiler are about one minute, and can be largely obviated. The H-compiler optimization should produce a program which runs in about 30% less CPU time, but some de-bugging probably has to be done before the logic is correct. A version of the simulation program in FORTRAN II compatible

with Smith's [5-3] executive program would also be desirable.

(e) No economic factors have been included in the simulation. If such factors are dealt with elsewhere, then the simulation program should at least print out a detailed analysis of all the backwash and regeneration events that have occurred during a run.

(VII-C) Long-Term Simulation Improvements

Certain features of the simulation cannot be improved without the acquisition of considerable quantities of new data, or extensive reprogramming. These are as follows:

(a) A sub-model is needed for the biological reactions along the lines of section (III-D). Ingenuity must be used in designing suitable experiments, because these effects will be masked by the more obvious adsorption and filtration effects.

(b) The backwashing equations used in Model I are rather naive. Some new theory and experiments are required.

(c) When the simulation has become somewhat more sophisticated, and the usual range of parameter values is well known, it would be desirable to add nonlinear parameter-fitting techniques to the simulation. At present, the program is given estimates of the parameters, and asked to simulate the column effluent. What is envisaged is the inverse procedure, where pilot plant data is read into the program and estimates of the parameters are called for. The number of rate parameters found in this manner cannot be reasonably be greater than four, due to the low statistical quality of the data. The search procedure should include an automatic modification of integration increment size. This simulation could then be used to analyze the behavior of carbon columns solely by means of effluent data.

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NOMENCLATURE

Symbol	Usage
b_1, b_2	parameters in Freundlich isotherm, Eq. (IV-3)
c	concentration of DOC
c_o	column inlet value of c at t = 0
C	dimensionless DOC concentration, Eq. (IV-22)
d_p	mean granule diameter
d_1	conversion factor, Eq. (III-6)
D_s	effective solid-phase diffusion coefficient
D_F	liquid-phase diffusion coefficient of adsorbate
f_1, f_2, .. f_7	unknown functions
k_ℓ, k_{ℓ_o}	liquid-phase mass transfer coefficients
k_{β_1}, k_{β_2}, k_{β_3}	biological rate constants, Eqs. (III-5, III-6, III-7)
K_o	filtration coefficient
k_s	solid-phase mass transfer coefficients
L	length of column
M	amount of DOC transferred to particle
N_1, . . N_4	dimensionless scale factors, Eqs. (IV-37, IV-38, IV-39, IV-40)
P	pressure
q	solid-phase concentration of adsorbate
q_o	initial value of q
Q	dimensionless solid-phase adsorbate concentration, Eq. (IV-23)
r_d	retention degradation of k_ℓ, Eq. (IV-28)
R_c, R_σ, S_2	rates for biological reaction
S_1	rate of particle deposition of filtration process

NOMENCLATURE (Cont'd.)

S	dimensionless retention, Eq. (IV-25)
t	time, characteristic coordinate
T	dimensionless time, Eq. (IV-30)
u, u_o	flow velocity
U, U_i	dependent variable
x_1, x_2	step sizes in z and t directions
y, y_o	suspended solids (SS) concentration
Y	dimensionless SS concentration, Eq. (IV-24)
z	spatial coordinate, characteristic coordinate
Z	dimensionless z, Eq. (IV-31)
δ, γ	pressure drop parameters
ε, ε_o	void fraction of bed (external to granules)
σ	retention, or deposited solids volumetric concentration
ρ_B	bulk density of dry carbon granules

APPENDIX A

(A:5) FORTRAN Listing of Simulation Program

```
//              (0451,CHE,45,40),'VANIER...FINIS'
// EXEC FORTGCLG,PARM.FORT='MAP',PARM.LKED='MAP'
//FORT.SYSIN DD *
C MPROG
C THIS PROGRAM SIMULATES THE PERFORMANCE OF A GRANULAR ACTIVATED
C CARBON COLUMN FOR WASTE WATER TREATMENT. THE MAIN PROGRAM
C READS INPUT DATA FOR THE SIMULATION, PRINTS A RECORD OF ALL
C PARAMETERS TO BE USED, AND CALLS UPON VARIOUS CALCULATION
C SUBROUTINES. THE MAIN ASSUMPTIONS OF THE SIMULATION ARE AS
C FOLLOWS :
C (1) THE COLUMN CAN BY REPRESENTED AS A CONTINUOUS MEDIUM. THUS
C     CONCENTRATIONS WITHIN THE COLUMN ARE SMOOTH FUNCTIONS OF
C     Z AND T, AND MEANINGFUL AVERAGE VALUES EXIST FOR PARTICLE
C     DIAMETER,VOID FRACTION,FLOW RATE,ETC.
C (2) PLUG FLOW EXISTS IN THE COLUMN. THUS, THE EFFECT OF RADIAL
C     CONCENTRATION GRADIENTS AND AXIAL DISPERSION IS ASSUMED TO
C     BE NEGLIGIBLE.
C (3) THE ORGANIC CONTAMINANTS IN THE WASTE WATER CAN BE
C     ADEQUATELY REPRESENTED BY THE TOTAL ORGANIC CARBON IN
C     SOLUTION ( TOC ), AND THE VOLUMETRIC SUSPENDED SOLIDS
C     CONCENTRATION ( SS ).
C (4) THESE CONCENTRATIONS ARE SMALL (DILUTE SOLUTION).
C (5) ISOTHERMAL CONDITIONS PREVAIL DURING THE SIMULATION.
C (6) INTRAPARTICLE CONCENTRATION GRADIENTS CAN BE REPRESENTED BY
C     AN AVERAGE SOLID CONCENTRATION AND SUITABLE SOLID PHASE MASS
C     TRANSFER EQUATIONS.
C (7) THE VOLUMETRIC FLOW RATE IS A FUNCTION OF TIME ONLY.
C (8) THE PHYSICAL PHENOMENA INVOLVED ARE ADSORPTION,DIFFUSION,
C     FILTRATION, AND BIOCHEMICAL REACTION.
C THESE 8 ASSUMPTIONS ARE INTERRELATED, AND IN SOME SENSE
C ESSENTIAL TO THE MODEL. A SECOND SET OF ASSUMPTIONS IS ADOPTED
C FOR SIMPLIFICATION, (BUT IS NOT ESSENTIAL)  :
C (A) THE MEAN  FLOW VELOCITY IS CONSTANT.
C (B) THE MEAN VOID SPACE IS CONSTANT.
C (C) THE BIOCHEMICAL EFFECTS ARE ABSENT.
C (D) BACKWASHING REMOVES A FIXED FRACTION OF THE PARTICLE SLIME
C     LAYER.
C (E) THE SLIME LAYER (RETENTION) CAUSES    THE LIQUID FILM MASS
C     TRANSFER COEFFICIENT TO DECREASE LINEARLY.
C (F) A QUADRATIC FREUNDLICH ISOTHERM REPRESENTS THE ADSORPTION
C     EQUILIBRIUM AT THE EXTERNAL PARTICLE SURFACE.
C (G) SOLID PHASE MASS TRANSFER IS GOVERNED BY A LINEAR GLUECKAUF
C     TYPE DRIVING FORCE EXPRESSION.
C (H) FILTRATION AND PRESSURE DROP PARAMETERS EVALUATED FOR AN
C     INITIALLY CLEAN BED CAN BE USED AFTER BACKWASHING AND SLIME
C     LAYER GROWTH.
C THE FOLLOWING SUBROUTINES ARE USED :
C    MOC     :  SOLVES PLUG FLOW EQUATIONS BY 3RD ORDER METHOD OF
C               CHARACTERISTICS AND PRINTS CONCENTRATION PROFILES.
C    BWASH   :  SIMULATES EFFECT OF BACKWASHING ON THE FIRST
C               SECTION OF THE COLUMN.
C    REGEN   :  REMOVES THE FIRST SECTION OF THE COLUMN AND
C               PLACES A FRESH SECTION AT THE END.
C    UZT     :  CHARACTERISTIC NORMAL ORDINARY DIFFERENTIAL
C               EQUATIONS (5) FOR ADSORPTION AND FILTRATION.
C    ZO      :  INITIALIZATION ALONG T=0 AXIS, AND AFTER EACH
C               BACKWASH. INTEGRATION BY 4TH ORDER RUNGE¬KUTTA
C               METHOD WITH RESPECT TO Z. (CALLED BY MOC )
C    TO      :  INITIALIZATION AT COLUMN INLET (Z=0). INTEGRATION
C               BY 4TH ORDER RUNGE¬KUTTA METHOD WITH RESPECT TO T.
C
```

```
C                (CALLED BY MOC)
C    UZ      :   SPECIAL FORM OF CHARACTERISTIC NORMAL EQUATIONS IN
C                C AND Y NEEDED ALONG T=CONSTANT. (CALLED BY ZO)
C    UT      :   SPECIAL FORM OF CHARACTERISTIC NORMAL EQUATIONS IN
C                Q AND S NEEDED ALONG Z=0.  (CALLED BY TO)
C ............INPUT DATA FORMAT.....................................
C USERS SHOULD READ THE FORTRAN 4 SPECIFICATIONS FOR NAMELISTS.
C ANY NUMBER OF SIMULATION RUNS CAN BE MADE CONSECUTIVELY, EACH
C RUN CORRESPONDING TO AN INPUT DATA SET. EACH INPUT DATA SET
C CONSISTS OF DESCRIPTIVE COMMENT CARDS FOLLOWED BY 4 NAMELISTS
C AS SHOWN BELOW :
C CARD (1)----STARTING IN COLUMN 1,
C CARBON
C CARDS (2),(3),...(N),          ANY FORMAT,
C ANY NUMBER OF COMMENT CARDS.
C CARD(N+1)--------STARTING IN COLUMN 1,
C ENDCOMMENT
C CARDS (N+2),(N+3),(N+4),(N+5), ETC,----STARTING IN COLUMN 2
C &FBP PB=?,UO=?,DP=?,VOIDS=?,L=?,NS=?, &END
C &OPCON CO=?,YO=?,SSCF=?, &END
C &REQP DS=?,KLO=?,FI=?,?,FC=?,?,?,RDKL=?,PRD=?,?,SRF=?, &END
C &CONTRL TBA=?,TPRINT=?,TMAX=?,KPX=?,DPMAX=?,CMAX=?,TREGEN=?,
C X=?,?,&END
C THE 4 NAMELISTS MUST BE IN THIS ORDER, BUT WITHIN A NAMELIST
C THE DATA MAY HAVE ANY ORDER. THE FIRST DATA SET MUST BE
C COMPLETE. THEREAFTER, ONLY THOSE PARAMETERS WHICH ARE TO BE
C CHANGED NEED BE MENTIONED IN FRESH DATA SETS. HOWEVER, DUE TO
C THE VAGARIES OF FORTRAN 4, EACH NAMELIST MUST CONTAIN AT LEAST
C ONE ELEMENT OF DATA. THE PROGRAM GIVES A DEFINITION OF THESE
C INPUT PARAMETERS WITH APPROPRIATE UNITS. SEE ALSO THE PH.D.
C DISSERTATION BY C.R.VANIER, S.U., 1970 . IN PARTICULAR, NOTE :
C---X(1) AND X(2) ARE THE INTEGRATION INCREMENTS IN SPACE AND
C TIME RESPECTIVELY. THESE ARE ADJUSTED BY THE PROGRAM SO THAT
C THEY ARE APPROPRIATE PROPER FRACTIONS OF L AND TBA. IF SPECIFIC
C TIME INCREMENTS ARE DESIRED, DEFINE TBA TO BE AN INTEGER
C MULTIPLE OF X(2). SIMILARLY, A SPECIFIC SPACE INCREMENT CAN BE
C OBTAINED BY ENSURING THAT L/NS IS AN INTEGER MULTIPLE OF X(1).
C EITHER THE FILTRATION OR THE ADSORPTION EFFECTS CAN BE
C EFFECTIVELY 'TURNED OFF' BY SETTING YO=0.0, OR CO=0.0 RESP.
C SOME TYPICAL INCREMENTS WHICH GIVE ABOUT 4 DECIMALS ACCURACY :
C FOR ADSORPTION : X(1)=1 FT, X(2)=32 HOURS (DS=2.5E-11 , KLO=5)
C FOR FILTRATION : X(1)=.25 FT, X(2)=.5 HOURS (FC=48,67,2.5)
C THESE ARE NOT GUARANTEED OUTSIDE OF THE PARAMETER RANGE INWHICH
C THEY WERE OBTAINED. NOTE THAT  THE FILTRATION EQUATIONS MAY
C DESTABILISE THE ADSORPTION EQUATIONS DUE TO COUPLING BY KLO .
C TPRINT AND KPX CONTROL THE EXTENT OF PRINTOUT AS FOLLOWS :
C---TPRINT---IS AN INTEGER WHICH SPECIFIES HOW MANY TIME-STEPS
C      MUST ELAPSE BETWEEN PROFILE PRINTOUTS.
C---KPX---IS AN INTEGER WHICH SPECIFIES THE NUMBER OF SPACE-STEPS
C      BETWEEN EACH ELEMENT OF U(I,J) TO BE PRINTED. THIS AFFECTS
C      COMBINED TOC PROFILES, COMPLETE PROFILE PRINTOUTS, AND
C      PROFILES AFTER BACKWASHING AND REGENERATION.
C TO SIMULATE COLUMNS WITH MORE THAN 100 SLICES, CHANGE THE
C SECOND DIMENSION FOR U,U1,U2,DU,DU1,DU2 EVERYWHERE THEY OCCUR.
C  (AND ALSO THE IF STATEMENT IN THE MAIN PROGRAM NUMBERED 111).
C.......... PROGRAM AUTHOR : CHRIS VANIER.......................
C..........SYRACUSE UNIVERSITY, CHEM ENG DEPT...................
C----------FORTRAN 4 VERSION-----------------------------------
      DIMENSION TITLE (16), COMENT(16)
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
```

```
      COMMON /PARM1/PB,UO,DP,VOIDS,L,NS
      COMMON /PARM2/CO,YO,SSCF
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      COMMON /KSS/XINC,KS,KLOK
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      REAL*4 KLO,N,L,KS,LSAVE
      INTEGER TPRINT
      DATA DUMMY/'AAAA'/,ENDC/'ENDC'/,CARB/'CARB'/
     ONAMELIST /FBP/PB,UO,DP,VOIDS,L,NS /OPCON/CO,YO,SSCF
     1          /REQP/DS,KLO,FI,FC,RDKL,PRD,SRF
     2          /CONTRL/TBA,TPRINT,TMAX,DPMAX,CMAX,X,TREGEN,KPX
      NRUN=0
C
C READ IN DATA
C
   10 READ(1,20,END=999,ERR=920) RCODE
   20 FORMAT(16A4)
      IF(RCODE.NE.CARB) GO TO 10
      NRUN=NRUN+1
      WRITE(3,30)NRUN
   30 FORMAT('1','CARBON COLUMN SIMULATION. RUN NO. ',I3/
     1 ' ',37('-')//)
   35 READ(1,20,ERR=920,END=999) COMENT
      IF(COMENT(1).EQ.ENDC)GO TO 50
      WRITE(3,40)COMENT
   40 FORMAT(' ',16A4)
      GO TO 35
   50 READ(1,FBP,ERR=920,END=999)
      READ(1,OPCON,ERR=920,END=999)
      READ(1,REQP,ERR=920,END=999)
      READ(1,CONTRL,ERR=920,END=999)
      XS2=X(2)
      X1SAVE=X(1)
      USAVE=UO
      LSAVE=L
      PSAVE=PRD(1)
      TBSAVE=TBA
      TSAVE=TREGEN
C
C CONVERT UNITS AND INITIALIZE
C
      JMAX= IFIX(L/( FLOAT(NS)*X(1)))+1
      IF(JMAX.EQ.(2*(JMAX/2))) JMAX=JMAX+1
      NSLICE=1+NS*(JMAX-1)
  111 IF(NSLICE.LT.100) GO TO 55
      WRITE(3,53) NSLICE
   53 FORMAT('ONUMBER OF SLICES = ',I10, /' CHANGE PROGRAM DIM',
     1 'ENSIONS OR CHOOSE A SMALLER L/X(2) RATIO'/)
      GO TO 920
   55 X(1)=1.0/ FLOAT(NSLICE-1)
      XINC=LSAVE*X(1)
      XS1=L*X(1)
      UO=UO*244.46
      L=L*30.48
      KLOK=0
      X(2)=TBA/ FLOAT( IFIX(TBA/X(2)))
      PRD(1)=PRD(1)*L
      X1CM=XS1*30.48
      X2MIN=XS2*60.0
      U(1,1)=1.0
```

```
      U(3,1)=1.0
      DO 15  J=1,NSLICE
      U1(5,J)=0.0
      U(5,J)=0.0
      DO 15 K=2,4,2
   15 U(K,J)=0.0
C
C LIST SIMULATION PARAMETERS
C
      WRITE(3,60)
   60 FORMAT('0FIXED BED PARAMETERS',/' ',20('-')/)
      WRITE(3,62) PB,UO,USAVE,DP,VOIDS,L,LSAVE,NS
   62 FORMAT(' BULK DENSITY OF CARBON (PB) = ',F7.4,
     1' GM/CM**3'/' MEAN SUPERFICIAL FLOW RATE (UO) = ',F7.2
     2,' CM/HR = ',F7.3,' GPM/FT**2'/,
     3' MEAN PARTICLE DIAMETER (DP) = ',F7.4,' CM'/
     4 ' VOID FRACTION OF BED = ',F7.4/
     5' TOTAL LENGTH OF COLUMN (L) = ',F8.2,' CM = ',F7.3,' FT'/
     6' NUMBER OF SECTIONS (NS) = ',I3//)
      WRITE(3,70)
   70 FORMAT('0OPERATING CONDITIONS',/' ',20('-')/)
      WRITE(3,72) CO,YO,SSCF
   72 FORMAT(' DISSOLVED TOC INPUT CONCENTRATION (CO) = ',E11.3,
     1 ' GM CARBON/CM**3 WASTE WATER'/
     2 ' SUSPENDED SOLIDS INPUT CONCENTRATION (YO) = ',E11.3,
     3 ' VOLUMES/VOLUME WASTE WATER'/
     4 ' SUSPENDED SOLIDS CONVERSION FACTOR (SSCF) = ',F8.3,
     5 ' GM TOC/CM**3 SUSPENDED SOLIDS'//)
      WRITE(3,80)
   80 FORMAT('0RATE AND EQUILIBRIUM PARAMETERS',/' ',31('-')/)
      WRITE(3,82) DS,KLO,FI,FC,RDKL,PSAVE,PRD(2),SRF
   82 FORMAT(' EFFECTIVE SOLID DIFFUSION COEFFICIENT (DS) = ',
     1 E12.4,' CM**2/SEC'/
     2 ' LIQUID FILM MASS TRANSFER COEFFICIENT FOR CLEAN GRANULE'
     3 ,'S (KLO) = ',E12.4,' 1/HR'/
     4 ' FREUNDLICH ISOTHERM PARAMETERS (FI) = ',2E12.4/
     5 ' NOTE : Q = FI(1)*C**FI(2)'/
     5 ' FILTER PARAMETERS = ',3E12.4/
     6 ' RETENTION DEGRADATION OF LIQUID FILM MASS TRANSFER COEF'
     7 ,'FICIENT (RDKL) = ',E12.4/ ' PRESSURE DROP PARAMETERS (P'
     8 ,'RD) = ',2E12.4,' ATM/CM, DIMENSIONLESS'/
     9  ' SLIME RESIDUE FACTOR (SRF) = ',F7.3//)
      WRITE(3,90)
   90 FORMAT('0CONTROL DATA FOR SIMULATION',/' ',27('-')/)
      WRITE(3,92) TBA,TREGEN,TPRINT,KPX,TMAX,DPMAX,CMAX,XS1,
     1XS2,X1CM,X2MIN
   92 FORMAT(' BACKWASH INTERVAL (TBA) = ',F7.1,' HRS'/
     1 ' REGENERATION TIME (TREGEN) = ',F7.1,' HRS'/
     1 ' PRINT EVERY ',I3,' TIME-STEPS AND EVERY ',I3,' SPACE-ST'
     1 ,'EPS'/
     2 ' SIMULATION INTERVAL (TMAX) = ',F8.1,' HRS'/
     3 ' PRESSURE DROP MAXIMUM (DPMAX) = ',E12.4,' ATMOSPHERES'/
     4 ' BREAKTHROUGH CONCENTRATION (CMAX) = ',E11.3,' GM TOC/CM'
     5 ,'**3'/' INTEGRATION INCREMENTS (X) = ',2E11.3,' FT, HRS'
     6 /' ',27X,'= ',2E11.3,' CM, MIN'//)
C
C CALCULATION OF DIMENSIONLESS SCALE FACTORS
C
      KS=15.0*DS*3600.0/DP**2
      X(2)=X(2)*KS
```

```
      TBA=TBA*KS
      TD=L*VOIDS/UO
      N(1)=L*KLO/UO
      IF(CO.NE.0.0) GO TO 94
      N(1)=0.0
      N(2)=0.0
      GO TO 96
   94 N(2)=KLO/(KS*PB*FI(1)*CO)
   96 IF(YO.NE.0.0) GO TO 97
      N(3)=0.0
      GO TO 98
   97 N(3)=L*FC(1)/UO
   98 N(4)=YO*FC(1)/KS
C
C EXECUTION PHASE
C
      WRITE(3,100) (N(J),J=1,4),KS,TD,NSLICE
  100 FORMAT(' SCALE FACTORS : ',4E13.5/
     1' EFFECTIVE SOLID MASS TRANSFER COEFFICIENT = ',E14.6,
     2' PER HR'/' DELAY TIME = HOLDUP = ',E14.6,' HRS'/
     3 ' NUMBER OF COLUMN SLICES = ',I5/)
      WRITE(3,110)
  110 FORMAT('1START OF SIMULATION'/)
      TIME=0.0
  120 CALL MOC(ISTOP)
      IF(ISTOP.EQ.1) GO TO 200
C
C NOTE THAT REGENERATION IS ASSUMED TO TAKE PRECEDENCE OVER
C BACKWASHING.
C
      IF(ISTOP.NE.2) GO TO 130
      CALL REGEN(JMAX)
      GO TO  120
  130 CALL BWASH(JMAX)
      GO TO 120
  200 WRITE(3,210)NRUN
  210 FORMAT('0END OF SIMULATION RUN ',I3)
C
C RESTORE USER VARIABLES
C
      UO=USAVE
      X(1)=X1SAVE
      X(2)=XS2
      L=LSAVE
      PRD(1)=PSAVE
      TBA=TBSAVE
      TREGEN=TSAVE
      GO TO 10
  999 WRITE(3,900)
  900 FORMAT('0END OF DATA')
 1000 STOP
  920 WRITE(3,930)
  930 FORMAT('0DATA ERROR.  CARDS SKIPPED'/)
      GO TO 10
      END
      SUBROUTINE MOC(ISTOP)
C
C U(1,J) = C , LIQUID PHASE SOLUBLE TOC
C U(2,J) = Q , SOLID PHASE ADSORBED TOC
C U(3,J) = Y , LIQUID PHASE SUSPENDED SOLIDS
```

```
C U(4,J) = S , SOLID PHASE DEPOSITED SOLIDS (RETENTION)
C U(5,J) = P , PRESSURE DIFFERENCE FROM INLET
C
      DIMENSION CHAR(5),Z(100)
      DIMENSION U2(5,100),DU(4,100),DU2(4,100),TOC(100)
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM2/CO,YO,SSCF
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      COMMON /KSS/XINC,KS,KLOK
      REAL*4 KLO,N,L,KS,LSAVE
      INTEGER TPRINT
      DATA CHAR/'C','O','Y','S','P'/
      IF(TIME.NE.0.0) GO TO 10
      X13=X(1)/3.0
      X23=X(2)/3.0
      X12=X(1)/2.0
      X22=X(2)/2.0
      X1M2=X(1)*2.0
      TREG=TREGEN
      XP=PRD(2)*X13
      DO 5 J=1,NSLICE
    5 Z(J)=XINC* FLOAT(J-1)
C
C INITIALIZATION ALONG T=0 AXIS
C
   10 T=0.0
      K=0
      CALL ZO
      DO 20 J=1,NSLICE
      DO 15 I=1,4
   15 U1(I,J)=U(I,J)
      CALL UZT(J)
      DO 20 I=1,4
   20 DU(I,J)=DU1(I,J)
C
C BOUNDARY CONDITION AT INLET
C
   27 K=K+1
      T=K*X(2)
      KLOK=KLOK+1
      TIME= X(2)* FLOAT(KLOK) /KS
      DO 120 J=2, NSLICE
      CALL TO
      CALL UZT(1)
C
C FIRST APPROXIMATION
C
   30 DO 40 I=1,3,2
      U1(I,J)=U1(I,J-1)+U(I,J)-U(I,J-1)+X(1)*(DU1(I,J-1)-
     1 DU(I,J-1))
   40 U1(I+1,J)=U1(I+1,J-1)+U(I+1,J)-U(I+1,J-1)+X(2)*(DU(I+1,J)-
     1 DU(I+1,J-1))
      CALL UZT(J)
C
C SECOND APPROXIMATION
C
      DO 60 I=1,3,2
      U1(I,J)=U1(I,J)+X12*(DU1(I,J)+DU(I,J-1)-DU1(I,J-1)-DU(I,J))
   60 U1(I+1,J)=U1(I+1,J)+X22*(DU1(I+1,J)+DU(I+1,J-1)-DU1(I+1,J-1
```

```
     1 )-DU(I+1,J))
       CALL UZT(J)
C
C APPLICATION OF SIMPSON'S RULE
C
       NJ=  1- (J-2*(J/2))
       IF(NJ)70,70,80
    70 DO 75 I=1,3,2
    75 U1(I,J)=U1(I,J-2)+X13*(DU1(I,J-2)+4.0*DU1(I,J-1)+DU1(I,J))
    80 NK= K-2*(K/2)
       IF(NK)90,90,100
    90 DO 95  I=2,4,2
    95 U1(I,J)=U2(I,J)+X23*(DU2(I,J)+4.0*DU(I,J)+DU1(I,J))
   100 IF((NJ.EQ.1).AND.(NK.EQ.1)) GO TO 120
       CALL UZT(J)
   120 CONTINUE
C
C PRESSURE CALCULATION
C NOTE THAT SINCE SIMPSON'S RULE IS USED FOR INTEGRATION,
C PRESSURES ARE ONLY GENERATED AT ALTERNATE POINTS (DO J).
C THE EVEN POINTS REMAIN AT THEIR INITIAL ZERO VALUE (ONE CAN,
C OF COURSE, INTERPOLATE). IF IT IS DESIRED TO BACKWASH
C INTERMEDIATE UNITS, THE PRESSURE PROFILES CAN  BE SCANNED
C IN THIS SUBROUTINE, AND APPROPRIATE LOGIC ADDED.
C
       DO 130 J=3,NSLICE,2
   130 U1(5,J)=U1(5,J-2)+ PRD(1)*(X1M2+XP*(U1(4,J-2)+4.0*U1(4,J-1)
      1 +U1(4,J)))
C
C STORAGE UPDATING
C
       DO 160 J=1,NSLICE
       DO 150 I=1,5
       U2(I,J)=U(I,J)
   150 U(I,J)=U1(I,J)
       DO 160 I=1,4
       DU2(I,J)=DU(I,J)
   160 DU(I,J)=DU1(I,J)
C
C COMBINED TOC (DISSOLVED+SUSPENDED) PRINTOUT
C
       WRITE(3,161)TIME
   161 FORMAT('0COMBINED TOC IN PPM AT TIME = ',F9.2,' HRS')
       DO 162 J=1,NSLICE
   162 TOC(J)=(U(1,J)*CO+SSCF*U(3,J)*YO)*1.0E6
       WRITE(3,163) (TOC(J),J=1,NSLICE,KPX)
   163 FORMAT( 5E15.6)
C
C LOGICAL CHECKS TO DETERMINE DETAILED PRINTOUTS, BACKWASHES,ETC
C
       IF(KLOK.NE.(TPRINT* (KLOK/TPRINT))) GO TO 180
       WRITE(3,181) TIME
   181 FORMAT('0DETAILED PROFILES',15X,'TIME = ',F8.3,' HRS'/' ',
      1 32X,19('-')/)
       WRITE(3,175) (Z(J),J=1,NSLICE,KPX)
   175 FORMAT(' Z (FEET)'/(     8F15.5))
       DO 166 I=1,5
       WRITE(3,169) CHAR(I)
   169 FORMAT(' ',A4)
   166 WRITE(3,167) (U(I,J),J=1,NSLICE,KPX)
```

```
167 FORMAT(8E15.6)
180 IF(TIME.LT.TMAX) GO TO 165
    ISTOP=1
    WRITE(3,190)
190 FORMAT('0SIMULATION TIME LIMIT REACHED')
    GO TO 300
165 IF(TOC(NSLICE).LT.(CMAX*1.0E6)) GO TO 200
    ISTOP=2
    WRITE(3,164)
164 FORMAT('0BREAKTHROUGH REACHED')
    GO TO 300
200 IF(U(5,NSLICE).LT.DPMAX) GO TO 230
    ISTOP=0
    WRITE(3,210)
210 FORMAT('0PRESSURE LIMIT REACHED')
    GO TO 300
230 IF(TIME.LT.TREG  ) GO TO 250
    TREG=TIME+TREGEN
    ISTOP=2
    WRITE(3,240)
240 FORMAT('0REGENERATION NEEDED')
    GO TO 300
250 IF(T.LT. TBA     ) GO TO 27
    ISTOP=0
    WRITE(3,170)
170 FORMAT('0BACKWASHING NEEDED')
300 RETURN
    END
    SUBROUTINE BWASH (JMAX)
C
C THIS SUBROUTINE IS A SOMEWHAT PRIMITIVE SIMULATION OF THE
C BACKWASHING PROCESS. IT IS ASSUMED HERE THAT ONLY THE FIRST
C SECTION IS BACKWASHED, AND A FIXED FRACTION IS REMOVED.
C NOTE THAT U(1,JMAX) IS PHYSICALLY EQUIVALENT TO 2 POINTS :
C THE EFFLUENT OF THE FIRST SECTION AND THE INFLUENT TO THE 2ND.
C AFTER BACKWASHING (OR ANY SECTION REARRANGEMENT) A DISCONTINUITY
C ARISES, AND THESE VALUES ARE PHYSICALLY DISTINCT AND UNEQUAL.
C IN THIS CALCULATION, THE BREAK IN U(4,J) IS SMOOTHED OVER.
C PROPERLY, THE TWO POINTS SHOULD HAVE BEEN STORED SEPERATELY,
C WHICH IMPLIES CALLING MUC FOR EACH SECTION IN TURN. IT IS NOT
C THOUGHT THATTHE DISCONTINUITY WILL HAVE AN APPRECIABLE EFFECT.
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      REAL*4 KLO,N,L
      DO 10 J=1,JMAX
   10 U(4,J)=SRF*U(4,J)
      WRITE(3,20)
   20 FORMAT('0BACKWASH COMPLETED. NEW S PROFILE :')
      WRITE(3,30) (U(4,J),J=1,NSLICE,KPX)
   30 FORMAT( 5E15.6)
      RETURN
      END
      SUBROUTINE REGEN(JMAX)
C
C THE FIRST SECTION OF THE COLUMN IS REMOVED FOR REGENERATION
C AND A SECTION OF FRESH CARBON IS ADDED TO THE END.  THIS
C SUBROUTINE TRANSFERS DATA FROM THE LOWER SECTIONS BY JMAX
C POSITIONS UP THE COLUMN, AND SETS TO ZERO THE SOLID PHASE
```

```
C CONCENTRATIONS U(2,J) AND U(4,J) IN THE BOTTOM SECTION.
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      DIMENSION CHAR(5)
      REAL*4 KLO,N,L
      INTEGER TPRINT
      DATA CHAR/'C','O','Y','S','P'/
      DO 10 J=JMAX,NSLICE
      K=J-JMAX+1
      U(2,K)=U(2,J)
      U(2,K)=U(2,J)
   10 U(4,K)=U(4,J)
      KMAX=NSLICE-JMAX+1
      DO 20 J=KMAX,NSLICE
      U(2,J)=0.0
   20 U(4,J)=0.0
      WRITE(3,30)
   30 FORMAT('OREGENERATED SECTION ADDED. 1ST SECTION DROPPED.'/)
      DO 50  I=2,4,2
   50 WRITE(3,40) CHAR(I),(U(I,J),J=1,NSLICE,KPX)
   40 FORMAT(' ',A1/(' ',5E15.6))
      RETURN
      END
      SUBROUTINE UZT(J)
C
C THIS SUBROUTINE IS THE HEART OF THE SIMULATION. IT CONTAINS
C THE MASS BALANCE AND RATE EQUATIONS FOR ALL COMPONENTS.
C DU(1,J) = DU1(1,J) = DC/DZ
C DU(2,J) = DU1(2,J) = DY/DZ
C DU(3,J) = DU1(3,J) = DQ/DT
C DU(4,J) = DU1(J,J) = DS/DT
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      REAL*4 KLO,N,L
      Y4=1.0-RDKL*U1(4,J)
      Y1=N(2)*Y4
      Y2=U1(1,J)-0.5*(-Y1+ SQRT(Y1*Y1+4*(U1(2,J)+Y1*U1(1,J))))
      Y3=U1(3,J)/(1+FC(2)*U1(4,J))**FC(3)
      DU1(1,J)=-N(1)*Y4*Y2
      DU1(2,J)=Y1*Y2
      DU1(3,J)=-N(3)*Y3
      DU1(4,J)=N(4)*Y3
      RETURN
      END
      SUBROUTINE TO
C
C VALUES MUST BE SUPPLIED FOR C(0,T) AND Y(0,T).
C ASSUME C=Y=1 AT Z=0, AND INTEGRATE OVER ONE TIME STEP.
C IN GENERAL, THE INPUT CONCENTRATIONS C=U1(1,1),AND Y=U1(3,1)
C MAY BE ARBITRARY FUNCTIONS OF TIME. THE FOLLOWING CODE ASSUMES
C THAT THEY DO NOT VARY FROM THEIR INITIAL VALUE OF UNITY.
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      REAL*4 KLO,N,L
      DIMENSION DF(4,2),Y(2) ,D(4)
      DATA D/1.0,2.0,2.0,1.0/
      X26=X(2)/6.0
```

```
      Y(1)=U(2,1)
      Y(2)=U(4,1)
      CALL UT (Y,DF,1)
      DO 20 I=2,4
      Y(1)= Y(1)+DF(I-1,1)*X(2)/D(I)
      Y(2)= Y(2)+DF(I-1,2)*X(2)/D(I)
   20 CALL UT(Y,DF,I)
      U1(2,1)=U(2,1)+X26*(DF(1,1)+2.0*(DF(2,1)+DF(3,1))+DF(4,1))
      U1(4,1)=U(4,1)+X26*(DF(1,2)+2.0*(DF(2,2)+DF(3,2))+DF(4,2))
      RETURN
      END
      SUBROUTINE UT(Y,DF,I)
C
C EVALUATION OF FUNCTIONS TO BE INTEGRATED ALONG Z=0 AXIS
C Y(1)=Q, Y(2)=S, DF(I,1)=DQ/DT, DF(I,2)=DS/DT
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      REAL*4 KLO,N,L
      DIMENSION Y(2),DF(4,2)
      Y1= 1-RDKL*Y(2)
      Y2=N(2)*Y1
      DF(I,1)=      Y2*(1.0-0.5*(-Y2+ SQRT(Y2*Y2+4*(Y(1)+Y2))))
      DF(I,2)=N(4)/(1+FC(2)*Y(2))**FC(3)
      RETURN
      END
      SUBROUTINE ZO
C
C INTEGRATION ALONG T=0  BY 4TH ORDER RUNGE-KUTTA METHOD.
C IT IS ASSUMED THAT Q(Z,0) AND S(Z,0) ARE KNOWN.
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM4/TBA,TREGEN,TMAX,DPMAX,CMAX,X(2),TPRINT,KPX
      REAL*4 KLO,N,L
      DIMENSION W(4,2),DF(4,2),      Y(2),D(4)
      DATA W /1.0,0.5,0.5,0.0,0.0,0.5,0.5,1.0/,D/1.0,2.0,2.0,1.0/
      X16=X(1)/6.0
      DO 40 J=2,NSLICE
      Y(1)=U(1,J-1)
      Y(2)=U(3,J-1)
      CALL UZ(J-1,W,Y,DF,1)
      DO 20 I=2,4
      Y(2)=U(3,J-1)+DF(I-1,2)*X(1)/D(I)
      Y(1)=U(1,J-1)+DF(I-1,1)*X(1)/D(I)
   20 CALL UZ(J-1,W,Y,DF,I)
      U(1,J)=U(1,J-1)+X16*(DF(1,1)+2*(DF(2,1)+DF(3,1))+DF(4,1))
   40 U(3,J)=U(3,J-1)+X16*(DF(1,2)+2*(DF(2,2)+DF(3,2))+DF(4,2))
      RETURN
      END
      SUBROUTINE UZ(J,W,Y,DF,I)
C
C EVALUATION OF FUNCTIONS TO BE INTEGRATED ALONG T=0 AXIS
C W IS A WEIGHTING FUNCTION FOR INTERPOLATION OF THE TABULATED
C VALUES OF Q=U(2,J) AND S=U(4,J). LINEAR INTERPOLATION IS USED.
C Y(1)=C, Y(2)=Y, DF(I,1)=DC/DZ, DF(I,2)=DY/DZ
C
      COMMON U(5,100),U1(5,100),DU1(4,100),N(5),TIME,NSLICE
      COMMON /PARM3/DS,KLO,FI(2),FC(3),RDKL,PRD(2),SRF
      REAL*4 KLO,N,L
      DIMENSION Y(2),W(4,2),DF(4,2)
```

```
      Y2 = W(I,1)*U(4,J)+W(I,2)*U(4,J+1)
      Y1=1.0 -RDKL*Y2
      Y3=N(2)*Y1
      DF(I,1)=-N(1)*Y1*(Y(1)-0.5*((-Y3)+ SQRT(Y3*Y3+4*(W(I,1)*
     1 U(2,J)+W(I,2)*U(2,J+1)+Y3*Y(1))))
      DF(I,2)= -N(3)*Y(2)/(1.0+FC(2)*Y2)**FC(3)
      RETURN
      END
/*
//GO.SYSIN DD *
CARBON
THIS DATA SET CORRESPONDS TO  NO.(6) IN TABLE (6-1)
EXTENDED CARBON COLUMN SIMULATION
REGULAR BACKWASHING-- NO PRESSURE BREAKTHRU ALLOWED
DATA COMES FROM JEFF'S COLUMN
DARCO CARBON AT 30 DEG.CENTIGRADE
ENDC
 &FBP
       UO=3.2,DP=.0648 ,VOIDS=.5,L=16.0,NS=1,PB=.39,
 &END
 &OPCON
  YO=10.0E-6, SSCF=1.0, CO=40.0E-6,
 &END
 &REQP
        KLO=100.0,FI=1.3541E9,2.0 ,FC=48.0,67.0,2.5, DS=4.0E-10,
          PRD=1.5E-3,283,SRF=.05,RDKL=10.0,
 &END
 &CONTRL
 TPRINT=12,TMAX=1200.0, DPMAX=3.00,CMAX=2.00E-6, TBA=96.0, KPX=2,
 TREGEN=5000.0,
  X=.50,2.0 &END
CARBON
NNNNNNN22222
ENDC
 &FBP NS=2 &END
 &OPCON SSCF=1.0 &END
 &REQP KLO=100.0 &END
 &CONTRL KPX=2 &END
CARBON
ENDCOMMENT
 &FBP NS=4 &END
 &OPCON SSCF=1.0 &END
 &REQP KLO=100.0 &END
 &CONTRL KPX=2 &END
CARBON
TEST  3333333
ENDCOMMENT
 &FBP NS=8 &END
 &OPCON SSCF=1.0 &END
 &REQP KLO=100.0 &END
 &CONTRL KPX=2 &END
CARBON
TEST  2222222222
ENDCOMMENT
 &FBP NS=16 &END
 &OPCON SSCF=1.0 &END
 &REQP KLO=100.0 &END
 &CONTRL KPX=2 &END
CARBON
THIS IS DATA SET NO(3) IN TABLE(6-1).
```

```
COMPARISON WITH PAYATAKES & MEHTER
RUN NO. 16, TABLES E8,E9 REFERENCE PAYATAKES
CARBON TYPE : DARCO 20*40 MESH, DXL-0-3892
ENDCOMMENT
 &FBP  UO=2.029,DP=.0594,VOIDS=.49,L=4.265092,NS=1,PB=.39,&END
 &OPCON  YO=88.2E-6,CO=0.0    ,SSCF=1.0 &END
 &REOP  FC=50.47,30.46,5.0950,PRD=.335E-3,464.1,KLO=100.0,DS=2.5E-11,
  SRF=.05,RDKL=10.0,FI=1.3451E9,2.0 &END
 &CONTRL  IPRINT=2,TMAX=2.00,X=.082021,.25,TBA=48.0,KPX=2,
 TREGEN=200.0 ,CMAX=1.0,
   DPMAX=1.0 &END
/*
```

APPENDIX B

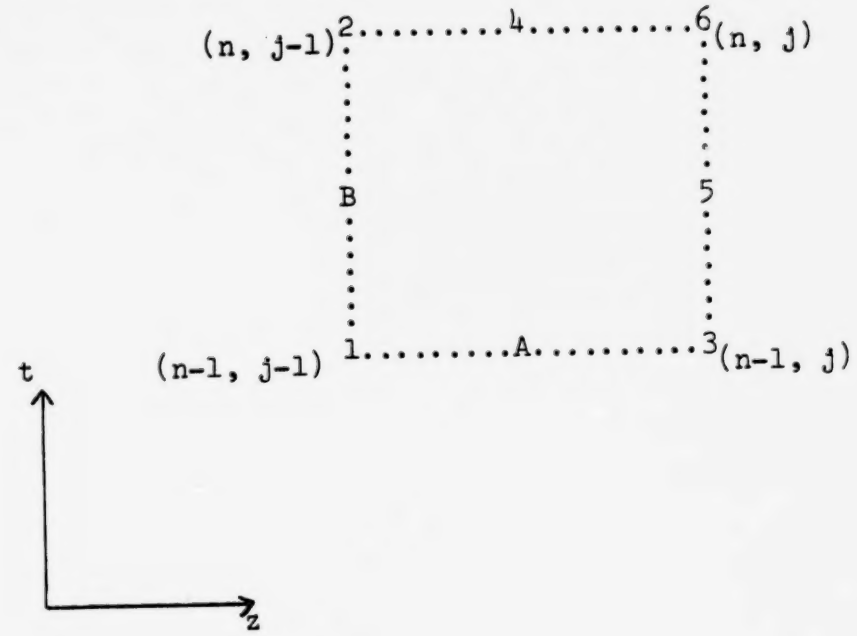
Algorithm for the Numerical Integration of Semi-Linear Hyperbolic Equations

The algorithm developed by Vanier and designated as CN553 for the numerical integration of semi-linear hyperbolic equations is briefly described as follows. Briefly, this algorithm is aimed at the solution of equations of the following type:

$$(U_1)_z = f_1 (z_1 t_1 U_1, U_2) \tag{A-1}$$

$$(U_2) = f_2 (z_1 t_1 U_1, U_2) \tag{A-2}$$

The algorithm has a basic integration step defined on a rectangle such as Fig. A-1



The basic grid spacing along the z direction is denoted by h and that along t is denoted as hθ, the subscripts (n,j), denotes the coordinates to be z = n·h t = (j)(hθ). It is assumed all the dependent variables and their derivatives are known as points 1, 2 and 3, and our purpose is to find U_1 and U_2 and their derivatives at point 6.

The basic algorithm can be described in terms of the following steps:

(a) Calculate values $U_1^{(3)}$ and $U_2^{(3)}$ by the following expressions:

$$U_1^{(3)} = U_{1j-1}^{n} + U_{1j}^{n-1} - U_{1j-1}^{n-1} + h\,(f_{1j-1}^{n} - f_{1j-1}^{n-1})^{\neq} \qquad \text{(A-3)}$$

$$U_2^{(3)} = U_{2j-1}^{n} + U_{2j}^{n-1} - U_{2j-1}^{n-1} + \theta h\,(f_{2j}^{n-1} - f_{2j-1}^{n-1})^{\neq} \qquad \text{(A-4)}$$

Note that $U_1^{(3)}$ and $U_2^{(3)}$ can be calculated directly, since it is assumed that values of U_1, U_2 are known at points 1, 2 and 3.

(b) If the values of $U_1^{(3)}$ and $U_2^{(3)}$ are taken as approximations of U_1 and U_2 at point 6, one can estimate the values of functions f_1 and f_2 at point 6, i.e:

$$f_{1j}^{n} = f_1(z_1 + h,\ t_1 + \theta h,\ U_1^{(3)},\ U_2^{(3)}) \qquad \text{(A-5)}$$

$$f_{2j}^{n} = f_2(z_1 + h,\ t_1 + \theta h,\ U_1^{(3)},\ U_2^{(3)}) \qquad \text{(A-6)}$$

(c) Based upon the values of $f_{1_j}^{n}$ and $f_{2_j}^{n}$, a fourth order approximation of U_1 and U_2 can be calculated:

$$U_1^{(4)} = U_1^{(3)} + \frac{h}{2}\,(f_{1j}^{n} + f_{1j-1}^{n-1} - f_{1j}^{n-1} - f_{1j-1}^{n}) \qquad \text{(A-7)}$$

$$U_2^{(4)} = U_2^{(3)} + \frac{\theta h}{2}\,(f_{2j}^{n} + f_{2j-1}^{n-1} - f_{2j}^{n-1} - f_{2j-1}^{n}) \qquad \text{(A-8)}$$

(d) Using $U_1^{(4)}$ and $U_2^{(4)}$ as approximations, one can evaluate f_{1n}^{j} and f_{2n}^{j} (i.e. repeating step b). Based on these new values

---

$^{\neq}$The superscript (3) denotes that the expression is of third-order approximation of the dependent variables U_1 and U_2.

of f_{1n}^{j} and f_{2n}^{j}, an improved value of U_1 at point 6 can be obtained according to:

$$U_{1j}^{n} = U_{1j-2}^{n} + \frac{h}{3}\left(f_{1j-2}^{n} + 4f_{1j-1}^{n} + f_{1j}^{n}\right) \qquad \text{(A-9)}$$

This step. however, is carried only for j being the odd number.

(e) Similarly, for U_2, the calculation is made according to:

$$U_{2j}^{n} = U_{2j}^{n-2} + \frac{\theta h}{3}\left(f_{2j}^{n-2} + 4f_{2j}^{n-1} + f_{2j}^{n}\right) \qquad \text{(A-10)}$$

for n being the odd number.

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27 Abstract A mathematical model has been devised to simulate the adsorption and filtration of waste water in an isothermal column packed with granular activated carbon. The adsorption process is considered to be controlled by a combination of liquid phase diffusion and interparticle diffusion which can be approximated by a solid phase rate expression based upon Glueckauf's Linear driving force. The filtration rate equation is assumed to be the same as that of filtration of clay suspension in a carbon bed, which was investigated experimentally as a companion study in this work. The effects of column backwashing and regeneration are also included in the model.

Abstractor Joseph F. Roesler | Institution EPA, WQO

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